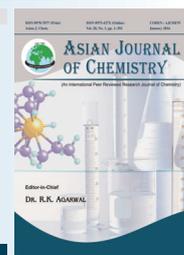




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## Use of Copper Slag Waste in Artistic Glazes Based on Li<sub>2</sub>O-ZnO System

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This paper presents the initial results of research on possibilities for utilization of copper smelting slag from Eti Bakir Kastamonu Küre Plant, Turkey for producing colourful crystal ceramic glazes. The compositions were formulated using the Seger method and applied in the commercial porcelain bodies which were fired at 1200 °C. Different amounts of wastes were added into the glaze compositions and applied in dry form to porcelain body. Suitable firing temperature was 1200 °C for 3 h. Copper smelting slag was characterized by XRD and DTA-TG. Glazes were characterized by SEM-EDX. The initial study has shown that copper smelting slag is suitable for obtaining artistic glazes based on Li<sub>2</sub>O-ZnO system and bringing the attractive colours to the ceramic glazes.

**Keywords:** Industrial wastes, Waste processing, Utilization, Artistic glazes.

### 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 resources 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 ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) under oxidizing conditions [14]. Glaze containing Li<sub>2</sub>O may show different crystallization behaviour since Li<sub>2</sub>O is a strong flux and can influence changes in the oxidation state of Fe<sub>2</sub>O<sub>3</sub> in the glaze. It has been reported that lithium metasilicate easily crystallized at low temperature in a Li<sub>2</sub>O-Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> glass. LiFeSi<sub>2</sub>O<sub>6</sub>, LiFe<sub>5</sub>O<sub>8</sub> and LiFeO<sub>2</sub> crystalline phases were formed during crystallization in CaO-MgO (Li<sub>2</sub>O, Fe<sub>2</sub>O<sub>3</sub>)-SiO<sub>2</sub> glasses. In the LiO<sub>2</sub>-ZnO-SiO<sub>2</sub> system, it was thought that Li<sub>2</sub>ZnSiO<sub>4</sub> phase developed due to the reaction of ZnO with Li<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>. A small addition of Li<sub>2</sub>O changes the crystallization path by precipitation of  $\beta$ -quartz

solid solution and Willemite at low temperature (800-900 °C). Doping of Li<sub>2</sub>O also stimulated the formation of Franklinite in Fe<sub>2</sub>O<sub>3</sub>-ZnO solid-solid interaction. However, it is still not clear which phases will form when Fe<sub>2</sub>O<sub>3</sub> is added to glazes containing Li<sub>2</sub>O and ZnO [14].

In this study, ceramic glazes containing Li<sub>2</sub>O-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 CS<sub>1</sub>, CS<sub>2</sub>, CS<sub>3</sub>, CS<sub>4</sub>, CS<sub>5</sub> and CS<sub>6</sub>, 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 °/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 with CuK<sub>α1</sub> radiation ( $\lambda = 1.5406 \text{ \AA}$ ) from 1.5° to 70° 2 $\theta$  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 (SiO<sub>2</sub>-ICDD 085-0335) pyrite (FeS<sub>2</sub>-ICDD71-1680) and chamosite (Mg<sub>5.036</sub>Fe<sub>4.964</sub>Al<sub>2.724</sub>(Si<sub>5.70</sub>Al<sub>2.30</sub>O<sub>20</sub>)(OH)<sub>16</sub>-ICDD 085-2163) (Fig. 1).

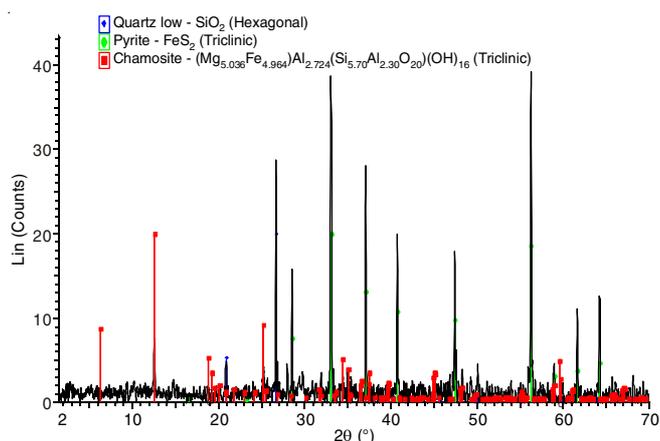


Fig. 1. X-ray diffraction patterns of copper slag

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

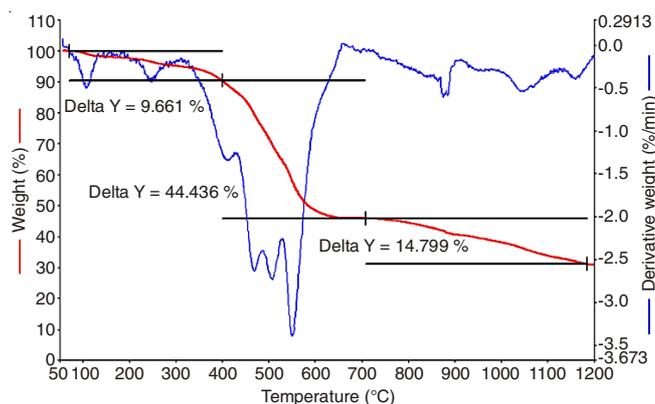


Fig. 2. Thermal analysis (DTA-TG) of the copper slag

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 about at 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 SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O, Li<sub>2</sub>O, ZnO, CaO, B<sub>2</sub>O<sub>3</sub> 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 with Na<sub>2</sub>O and B<sub>2</sub>O<sub>3</sub> content.

The aesthetic appearance of the glazes is significant (Fig. 3). For instance, after the firing at 1200 °C, all of the glazes exhibit greenish to brown colour an extensive re-crystallization due to the addition of large amount of iron oxide from copper slag. The colour of glazes is strongly dependent on the amount of copper slag, the ratio of Fe<sup>2+</sup>/Fe<sup>3+</sup> in glaze matrix and the chemical composition of base glaze.

SEM micrographs and EDX patterns of CS<sub>1</sub>, CS<sub>2</sub>, CS<sub>3</sub>, CS<sub>4</sub>, CS<sub>5</sub> and CS<sub>6</sub> glazes are shown in Figs. 4-9, respectively.

TABLE-1  
CHEMICAL COMPOSITION wt % OF COPPER SLAG

Oxides (wt, %)									
SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	CuO	MnO	ZnO
28.63	6.77	57.40	0.30	1.24	0.32	0.81	0.96	0.08	0.20



Fig. 3. Surface appearance and colour of the glazes prepared by copper slag fired at 1200 °C; CS<sub>1</sub>, CS<sub>2</sub>, CS<sub>3</sub>, CS<sub>4</sub>, CS<sub>5</sub> and CS<sub>6</sub>

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. CS<sub>2</sub> and CS<sub>6</sub> glazes were needed to be gloss

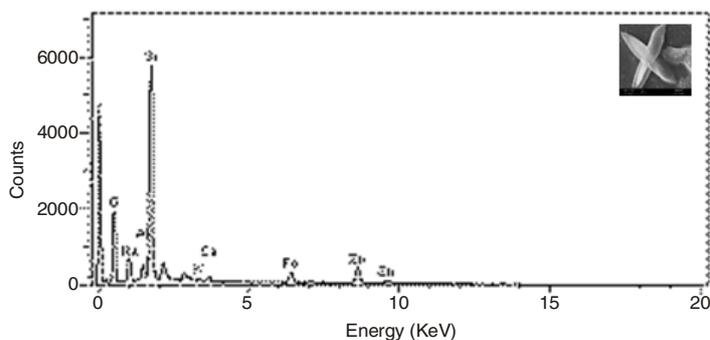
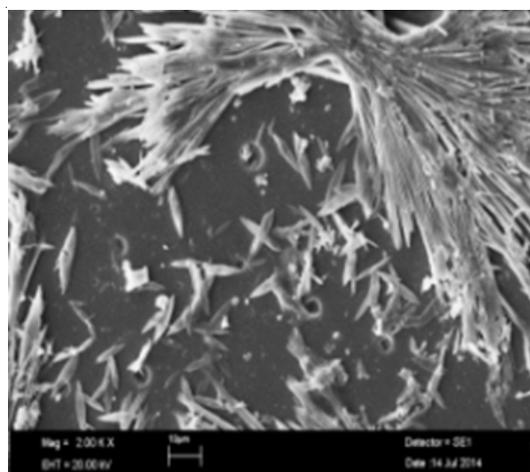


Fig. 4. SEM micrograph of the CS<sub>1</sub> glaze and EDX pattern taken from the crystal occurrence

TABLE-2 MOLECULAR FORMULA OF CERAMIC GLAZES CS <sub>1</sub> , CS <sub>2</sub> , CS <sub>3</sub> , CS <sub>4</sub> , CS <sub>5</sub> AND CS <sub>6</sub>				
Code	Basic Oxides	Neutral oxides	Acid oxides	Waste material
CS <sub>1</sub>	0.40 Na <sub>2</sub> O 0.20 Li <sub>2</sub> O 0.40 ZnO	0.20 Al <sub>2</sub> O <sub>3</sub>	2.00 SiO <sub>2</sub> 0.75 B <sub>2</sub> O <sub>3</sub>	15 % copper slag
CS <sub>2</sub>	0.50 Li <sub>2</sub> O 0.50 ZnO	0.30 Al <sub>2</sub> O <sub>3</sub>	1.6 SiO <sub>2</sub> 1.0 B <sub>2</sub> O <sub>3</sub>	15 % copper slag
CS <sub>3</sub>	0.40 Li <sub>2</sub> O 0.30 CaO 0.30 ZnO	0.25 Al <sub>2</sub> O <sub>3</sub>	1.20 SiO <sub>2</sub> 0.75 B <sub>2</sub> O <sub>3</sub>	15 % copper slag
CS <sub>4</sub>	0.40 Na <sub>2</sub> O 0.30 Li <sub>2</sub> O 0.30 ZnO	0.15 Al <sub>2</sub> O <sub>3</sub>	2.00 SiO <sub>2</sub> 0.75 B <sub>2</sub> O <sub>3</sub> 2.00 TiO <sub>2</sub>	15 % copper slag
CS <sub>5</sub>	0.45 Na <sub>2</sub> O 0.25 Li <sub>2</sub> O 0.30 ZnO	0.20 Al <sub>2</sub> O <sub>3</sub>	1.2 SiO <sub>2</sub> 1.0 B <sub>2</sub> O <sub>3</sub>	15 % copper slag
CS <sub>6</sub>	0.70 Li <sub>2</sub> O 0.30 ZnO	0.30 Al <sub>2</sub> O <sub>3</sub>	1.80 SiO <sub>2</sub> 0.75 B <sub>2</sub> O <sub>3</sub>	15 % copper slag

fired in the high temperature range of 1300-1350 °C. Their surfaces were unmaturred related to the high levels of Al<sub>2</sub>O<sub>3</sub>. 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 Li<sub>2</sub>O-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> 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.

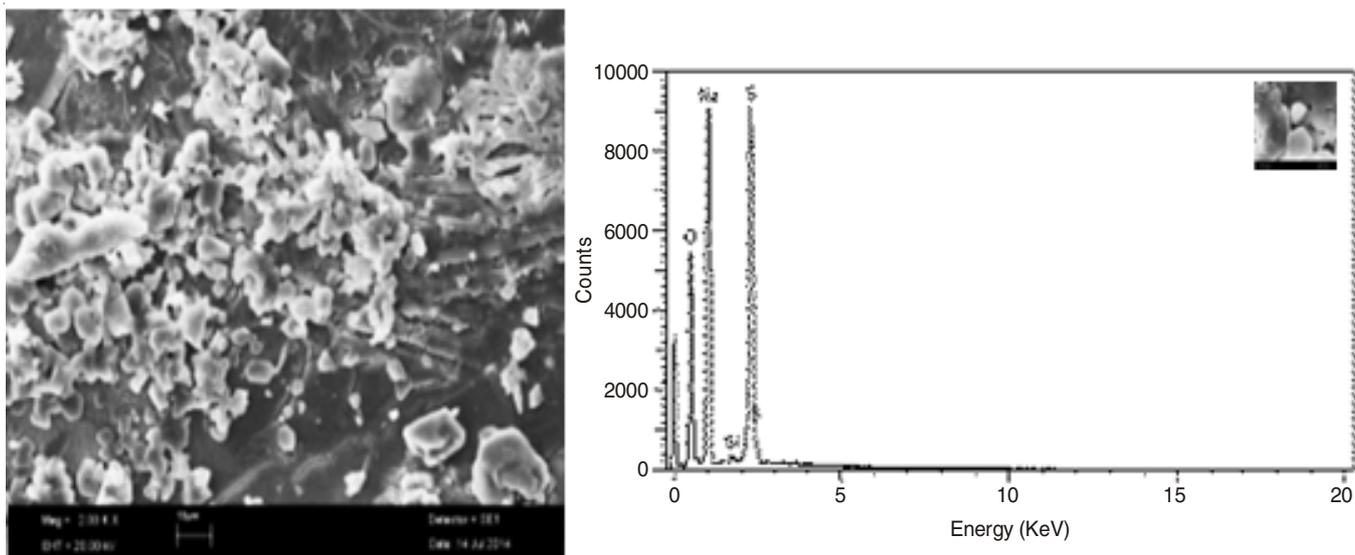


Fig. 5. SEM micrograph of the CS<sub>2</sub> glaze and EDX pattern taken from the crystal occurrence

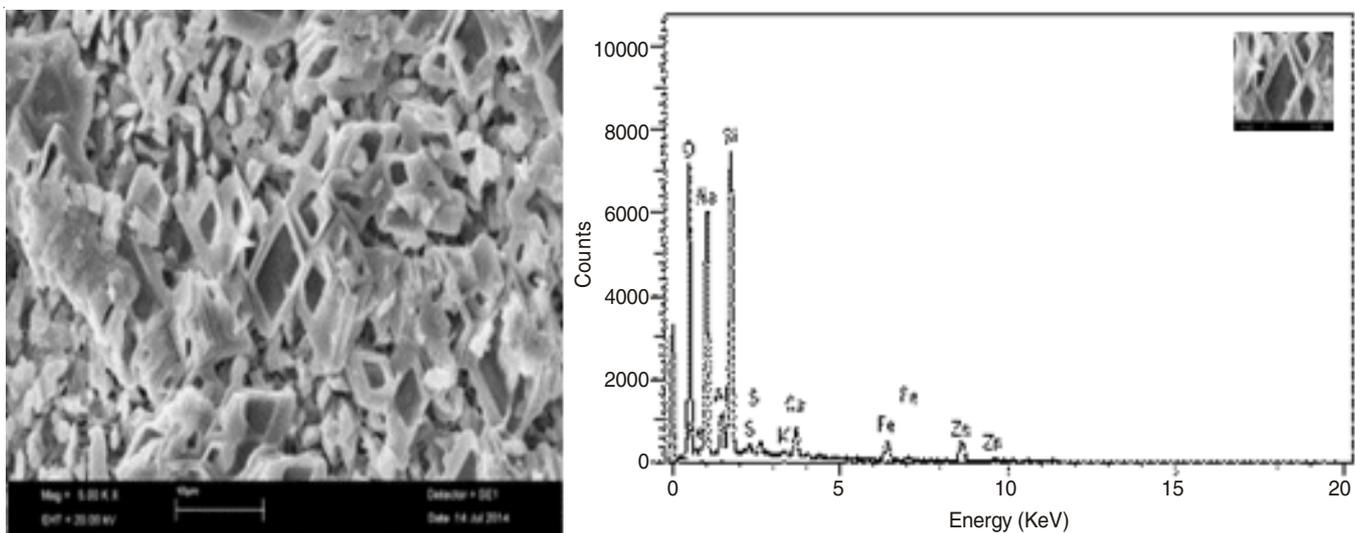


Fig. 6. SEM micrograph of the CS<sub>3</sub> glaze and EDX pattern taken from the crystal occurrence

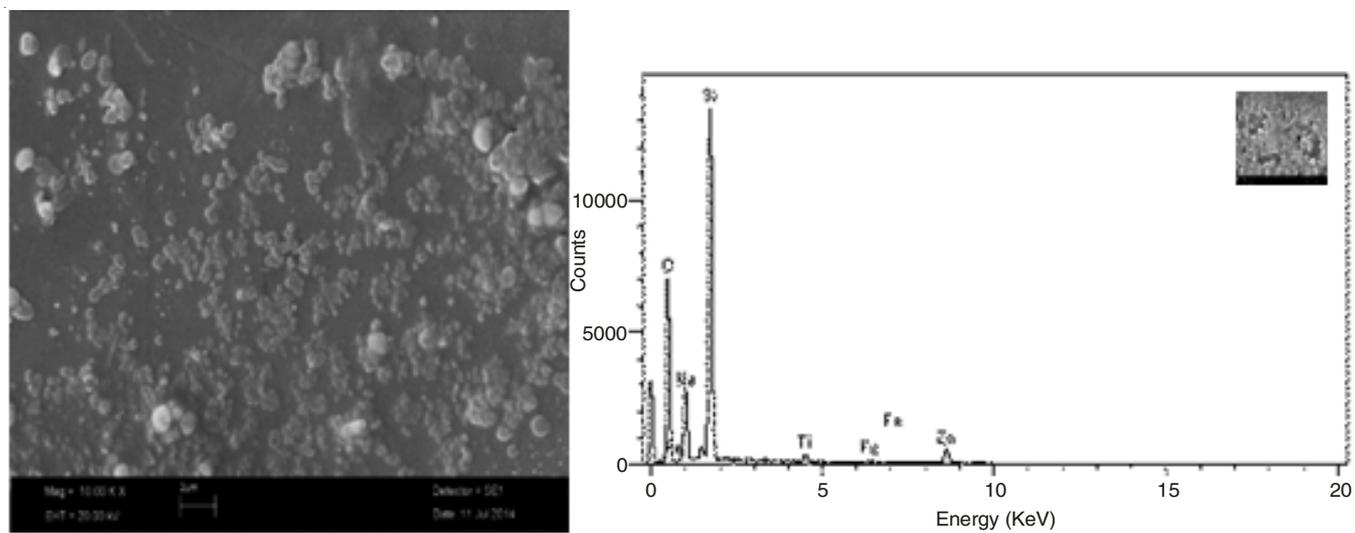


Fig. 7. SEM micrograph of the CS<sub>4</sub> glaze and EDX pattern taken from the crystal occurrence

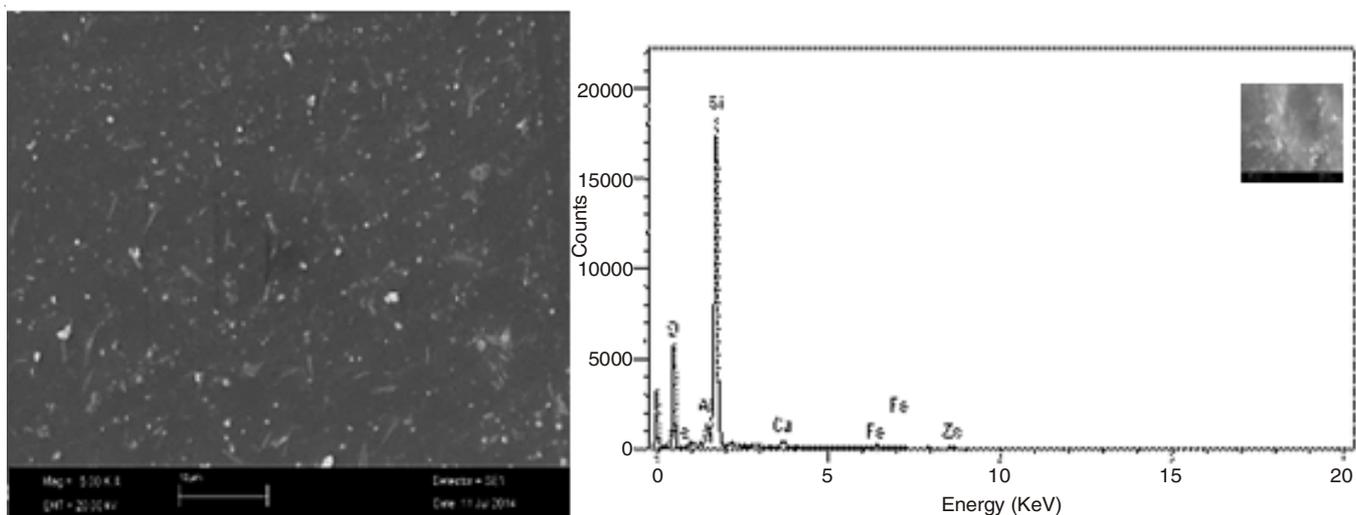


Fig. 8. SEM micrograph of the CS<sub>5</sub> glaze and EDX pattern taken from the crystal occurrence

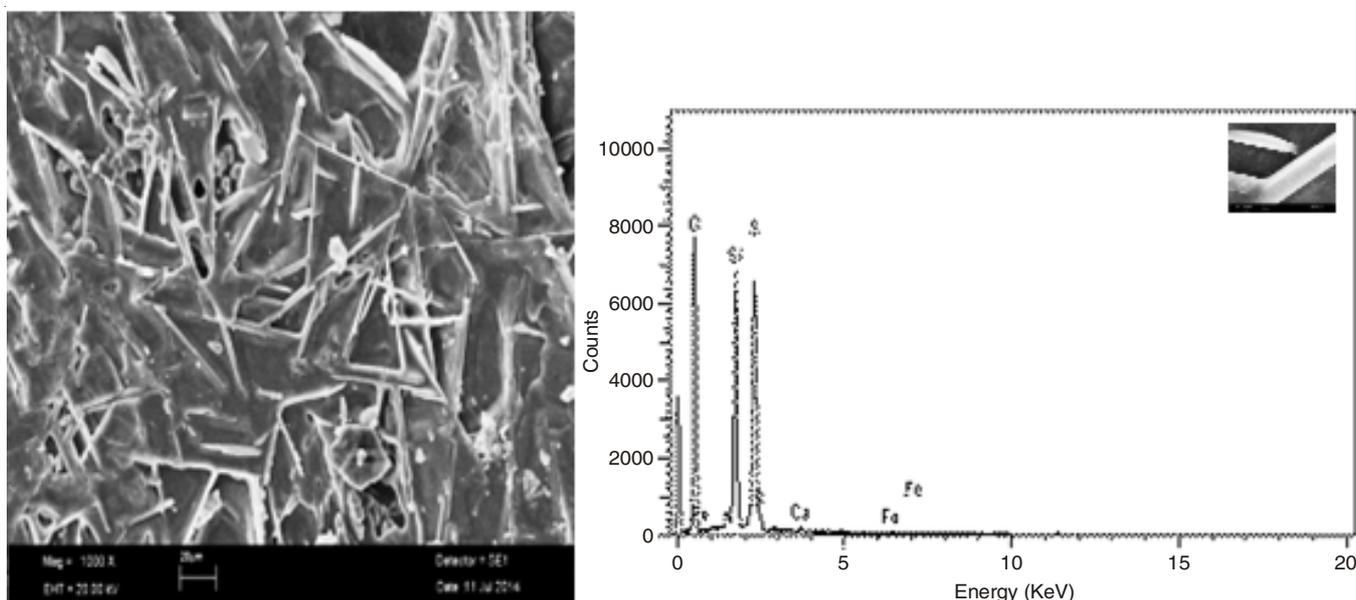


Fig. 9. SEM micrograph of the CS<sub>6</sub> glaze and EDX pattern taken from the crystal occurrence

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