An investigation of color development by means of the factorial design in wall tile glazes with ferrochromium fly ash

Zahide Bayer Öztürk*, Burçak Atayb, Münevver Çakić & Nuran Ayd

aMetallurgical and Materials Engineering Department, Nevşehir Hacı Bektaş Veli University, 50300, Nevşehir, Turkey
bEczacıbaşı Karo Seramik, Bozüyük, Eskisehir, Turkey
cDepartment of Ceramic Arts, Anadolu University, 26470, Eskisehir, Turkey
dDepartment of Materials Science Engineering, Anadolu University, 26555, Eskisehir, Turkey

Received 20 September 2013; accepted 25 September 2014

In tile manufacturing, generally different glazes with 1-15 wt% pigment and dye are used to obtain aesthetic properties. It can be said that pigment and dyes are the most expensive raw materials in glaze production due to its high costs limits. Ferrochromium fly ashes are a waste material obtained from the manufacturing of ferrochromium alloy. It mainly consists of chrome, ferric oxides, CaO and also MgO and Al₂O₃. This study outlines a novel approach in formulating tile glaze production as coloring agent. With this aim factorial design of experiment is used for defining the main factors on color formation. These factors are calcination temperature of fly ash, amount of fly ash and type of glaze. Ferrochromium fly ash is calcined at 1000, 1100 and 1160°C for 6 h and added at 1-4 wt% to transparent, opaque and matt glaze compositions. Glazed wall tiles were sintered at 1145°C for 30 min. For comparison of the colorimetric parameters (L*, a*, b*) of glazes spectrometer is used. The crystalline phases of the obtained glazed samples and fly ashes which calcined at different temperatures and different type glazes are evaluated by X-ray diffraction and scanning electron microscopy (SEM, EDS), respectively. Different brown tones are observed related to zinc iron chromite spinel crystal structure in glazed wall tiles. The most effective factors are determined by factorial design as amount of fly ash for L* parameter, and glaze type for a*, b* parameters.

Keywords: Ceramic tile, Factorial design, Fly ash, Glaze

Ceramic tiles are heterogeneous materials, consisting mainly of natural raw materials with wide range in composition. Thus, these products can tolerate the substitution of different types of waste materials rather well, even in high amounts. In recent years, recycling of industrial wastes has gained great attention and became a major challenge for environmental solutions by reducing natural environment pollution as contamination of soil, water and air. The usage of these wastes by incorporation into a productive cycle represents many advantages as providing alternative raw material resource for many industries, reducing production costs and saving energy. The earlier studies have focused evaluation of huge waste (post-treated incinerator bottom ash) obtained of new ceramics and permitted to establish a better sinter-crystallization ability for new glass formulation.

Ferrochromium fly ash is a waste material existing in large scales during production of power plants which includes high amount of Cr₂O₃, Fe₂O₃ and used for cement, brick and ceramic artware industries as a raw material. Chromium and iron compounds are well known coloring materials especially in ceramic industry. In ceramic tile production, coloring agents are used at body and glaze alone or with other oxides. In this regard, recycling of fly ashes as a raw material for colored ceramic tiles which are mainly manufactured at large scales would be a challenge for ceramic tile industry by reducing cost and providing the recovery of these wastes due to the application of its high amount of chromium and iron ingredients.

There are many factors affecting the quality and technical performances of processing during production, such as raw material selection, process equipments, etc. in ceramic industry. In order to determine the main factors influencing the characteristics of the product, experimental design methods are used. It is created by mathematical models and used to survey of qualification and determination of output and also its effectiveness.

*Corresponding author: (E-mail: z.ozturk@nevsehir.edu.tr)
One of the experimental design methods is factorial design in which all combinations of the examined factors can be investigated. A designed experiment will promote the determination of suitable conditions to achieving process optimization. The interactions between the factors could be determined with appropriate experiments defined by factorial design. Confidence and effective results are achieved by using less labor and time with factorial design of experiment. In literature many researches have pointed out the benefits of factorial design of experiments for determining the factors influencing the various production steps of ceramic manufacturing. In this study, ferrochromium fly ash which is the waste of arc furnace used for production of steel and chromium at Antalya Ferrochromium plant in Turkey was used as raw and calcined form in wall tile glazes and the effect of usage on color parameters was investigated by using the factorial design of experiment.

Aim of this study was to prepare conventional colored glaze by utilizing this waste ferrochromium fly ash as raw and calcined form instead of pigments and dyes for ceramic glazes. They were characterized by X-ray diffraction (XRD) and secondary electron microscopy (SEM) for structural changes and evolution of new phases. The recycling and the utilization of this waste as coloring agent for glaze production will provide economical and environmental benefits to country.

**Experimental Procedure**

The chemical composition of ferrochromium fly ash having particle size distribution below 1 mm is reported in Table 1. The fly ash was also calcined at 1000, 1100 and 1160°C for 6 h with the main scope of sealing several pollutants in a higher chemically stable material. Generally, the pigments produced according to the actual process are inorganic compounds that can then be added to vitreous or ceramic matrixes, give them a uniform color without altering their common physical properties. The aim of calcination of fly ash in different temperatures such as the pigment structure should remain insoluble and unreactive upon firing in order to give a homogeneous coloration to the glaze. Furthermore, in order to establish a better understanding how calcined and raw fly ash addition effects the variation of color in wall tile glazes. The calcined and raw fly ashes were added to transparent, opaque and matt glaze (1-4 wt%). Chemical compositions of the wall tile glazes were determined by using Seger formulation in Table 2. Glaze compositions containing fly ash of both raw and calcined, dry glaze (200 g), sodium tripolyphosphate-STPP (0.4 g) were prepared by wet milling (100 g water, 20 min) using a laboratory ball mill (residue < 2%, at 45 µm). The glazes at 1650 g/L were applied on 250×200×8 mm the wall tiles and fired in the industrial roller kiln (1145°C for 30 min). The factors used for factorial design method were selected as calcination temperature of fly ash, amount of fly ash and type of glaze. These factors and their interactions were given in Tables 3 and 4.
respectively. When Table 3 examined, two factors with four levels and a factor with three levels were given and 48 samples are prepared according to $4^2 \times 3^1$ mixed level factorial design. The chromatic coordinates of the fired samples were measured by means of a Minolta CR-300 series chromometer. X-ray diffraction measurements were carried out on glaze surface in 5-70°, 2θ range using a diffractometer (Rigaku Rint 2200). The microstructure of glazed tiles was observed by scanning electron microscopy (Zeiss Supra 50 VP and FEI Nova Nanosem 650 equipped with EDS).

**Results and Discussion**

$L^*$, $a^*$ and $b^*$ parameters show whiteness, red or green and yellow or blue color tendency, respectively. The color parameters ($L^*$, $a^*$, $b^*$) values of 48 samples which were prepared according to $4^2 \times 3^1$ mixed level factorial designs were measured. The factors and their interactions were analyzed with ANOVA table (the analysis of variance). The table provides to understand the difference among the factor levels and to determine whether their interactions are meaningful. In the ANOVA table which includes the effective main factors and their interactions in Table 5 according to $L$ value DF is degrees of freedom, Seq SS is sum of squares, MS is square, $F$ distribution is used to determine the differences between factor variances. So the largest $F$ value is the most effective factor in the model. $P$ values indicating the ratio of the unadmitted region ($P$ values which are lower than the admitted $\alpha$ are effective). $\alpha = 0.01$ value is used (with 99 % confidence interval).

![Fig. 1 – Main effects plots for $L^*$ value](image1.png)

![Fig. 2 – Pie chart for $L^*$ value](image2.png)

**Table 4 – Main factors and their interactions**

<table>
<thead>
<tr>
<th>Main factors</th>
<th>Two factor interactions</th>
<th>Three factor interactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcination temperature of fly ash (°C)</td>
<td>Calcination temperature of fly ash (°C)* Amount of fly ash (wt%)</td>
<td>Calcination temperature of fly ash (°C)* Amount of fly ash (wt%)* Type of glaze</td>
</tr>
<tr>
<td>Amount of fly ash (wt%)</td>
<td>Calcination temperature of fly ash (°C)* Type of glaze</td>
<td>Amount of fly ash (wt%)* Type of glaze</td>
</tr>
<tr>
<td>Type of glaze</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 5 – ANOVA table of $L^*$ value for effective factors**

<table>
<thead>
<tr>
<th>Factors</th>
<th>DF</th>
<th>Seq SS</th>
<th>MS</th>
<th>$F_0$</th>
<th>$P$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amount of fly ash (wt%)</td>
<td>3</td>
<td>1847.66</td>
<td>615.89</td>
<td>91.26</td>
<td>0.000</td>
</tr>
<tr>
<td>Type of glaze</td>
<td>2</td>
<td>1748.96</td>
<td>874.48</td>
<td>129.58</td>
<td>0.000</td>
</tr>
<tr>
<td>Error</td>
<td>42</td>
<td>283.44</td>
<td>6.75</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Total</td>
<td>47</td>
<td>3880.05</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Main factors and their interactions whose effectiveness are meaningful are added to ANOVA table error term. If the value $P$ of main effect and the interactions of the factor is higher than 0.01, this interaction and effects are added to the error table. For this reason, only effective factors are cited in Anova table for investigated result.

The interaction graphs of effective factors and pie chart for $L^*$ value were given in Figs 1 and 2. The
lightness of glazed wall tiles, $L^*$ value was decreased by increasing amount of fly ash in glaze compositions. The reason of decreasing at $L^*$ values was Fe$_2$O$_3$ and Cr$_2$O$_3$ content of fly ash. The fly ash amount at 47.6% is the effective factor. It was observed that the second effective factor as 45.1% which was the type of glaze also influences the $L^*$ value. The error factor was defined 7.3% and the interaction factors, the calcination temperature from main factors higher than $P=0.001$.

As seen from Table 6, the $a^*$ values were sensitive to all of main factors as calcination temperature of fly ash (°C), amount of fly ash (wt%) and type of glaze. The $a^*$ value was increased in the third and forth level of calcination temperature of fly ash and amount of fly ash factors. The increment at $a^*$ value was due to the Fe$_2$O$_3$ content of fly ash$^{21}$. Type of glaze with 48.7%, amount of fly ash with 27.2%, calcination temperature of fly ash with 7.6% were significant factors for $a^*$ values (Fig. 3) and these factors constitutes 83.5% of total effect. The remaining part was composed of error factor which is determined by adding other factors higher than $P=0.001$ to error.

The main effects of each factor and their interactions were given in Table 7 for $b^*$ values. For $b^*$ values; type of glaze as 73.9%, calcination temperature as 11.8%, the interaction between the amount of fly ash and glaze type as 7.1% and the amount of fly ash as 1.9% were main factors and constitute the 94.7% of total factors. At calcination temperatures of fly ash levels from second to third and fourth levels $b^*$ values were increased. At all levels of fly ash amount and also at first, second level of glaze type, while there was no significant change at $b^*$ values, at third level of glaze type $b^*$ values start to go up (Fig. 4) which was due to the lack of crystal phase at transparent glaze which could cause the variations at colorimetric parameters. Figure 5 shows the interaction factor between the amount of fly ash and glaze type.

### Table 6 – ANOVA table of $a^*$ value for effective factors

<table>
<thead>
<tr>
<th>Factors</th>
<th>DF</th>
<th>Seq SS</th>
<th>MS</th>
<th>$F_0$</th>
<th>$P$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcination temperature of fly ash (°C)</td>
<td>3</td>
<td>7.449</td>
<td>2.483</td>
<td>5.99</td>
<td>0.002</td>
</tr>
<tr>
<td>Amount of fly ash (wt%)</td>
<td>3</td>
<td>26.690</td>
<td>8.897</td>
<td>21.47</td>
<td>0.000</td>
</tr>
<tr>
<td>Type of glaze</td>
<td>2</td>
<td>47.753</td>
<td>23.876</td>
<td>57.62</td>
<td>0.000</td>
</tr>
<tr>
<td>Error</td>
<td>39</td>
<td>16.161</td>
<td>0.414</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Total</td>
<td>47</td>
<td>98.053</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

### Table 7 – ANOVA table of $b^*$ value for effective factors

<table>
<thead>
<tr>
<th>Factors</th>
<th>DF</th>
<th>Seq SS</th>
<th>MS</th>
<th>$F_0$</th>
<th>$P$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcination temperature of fly ash (°C)</td>
<td>3</td>
<td>75.80</td>
<td>25.267</td>
<td>24.27</td>
<td>0.002</td>
</tr>
<tr>
<td>Amount of fly ash (wt.%)</td>
<td>3</td>
<td>12.102</td>
<td>4.034</td>
<td>3.88</td>
<td>0.018</td>
</tr>
<tr>
<td>Type of glaze</td>
<td>2</td>
<td>474.132</td>
<td>237.066</td>
<td>227.76</td>
<td>0.000</td>
</tr>
<tr>
<td>Amount of fly ash* type of glaze</td>
<td>6</td>
<td>45.313</td>
<td>7.552</td>
<td>7.26</td>
<td>0.000</td>
</tr>
<tr>
<td>Error</td>
<td>33</td>
<td>34.348</td>
<td>1.041</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Total</td>
<td>47</td>
<td>641.695</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
for $b^*$ value. It was observed that for transparent glaze (glaze type 3), the increase at the amount of fly ash (level 4) cause rising of $b^*$ values which was expected due to the increasing level of Fe$_2$O$_3$ content.

The optical properties of glazes are depending on the reflectance and scattering of light from irregular seeds or crystals in glaze\textsuperscript{22}. While the crystal phases are getting developed in glaze, different surface structures from transparent to opaque or from opaque to matt could be formed\textsuperscript{23}. At matt and opaque glazes the intensity of incident light and diffraction changes due to the crystals in the glaze, but at transparent glazes incident light is not exposed to any change as in reflectance or scattering\textsuperscript{24}. Because of these differences the color at matt, opaque glazes exhibits lightness hue when compared with transparent glazes (Fig. 6).

In order to investigate these differences experimentally, 1% raw fly ash added matt, opaque and transparent glazes were analyzed by using XRD to observe the crystal phase formations. At matt glazes the crystal phases are zircon (ZrSiO$_4$), sanidine ((K,Na)(Si$_3$Al)O$_8$), quartz (SiO$_2$), and at opaque glaze the crystal phases zircon, orthoclase (KAlSi$_3$O$_8$), quartz, fayalite (Fe$_2$SiO$_4$) were detected, for transparent glaze only quartz has been assigned (Fig. 7).

The XRD diffractograms of calcined and raw fly ashes revealed a chromite, hematite and amorphous nature (Fig. 8). In the SEM studies (Figs 9-11), an opaque glaze reveals the presence of crystalline phase with an acicular structure typical of zircon. A matt glaze clearly reveals the presence of crystalline phases with zircon and with a small grain structure of the zinc iron chromite brown spinel crystal structure. But transparent glaze not reveals any crystalline phases.

\begin{equation}
\text{(Fe,Cr)}_2\text{O}_3 \text{ (hematite)} + \text{ZnO (from glaze)} = \text{Zn (Fe,Cr)}_2\text{O}_4 \text{ (spinel)} \ \cdots \ (1)
\end{equation}

This equation illustrated that when hematite and chromite crystal phases are placed in a zinc oxide-containing glaze, it will react with the zinc oxide to form in place a zinc iron chromite brown spinel pigment. This situation might be due to the zinc in the glaze to
Fig. 7 – XRD graphs of glazes

Fig. 8 – XRD graphs of fly ash calcined at different temperatures

Fig. 9 – SEM micrograph of opaque glaze containing 1 wt% raw ash and EDS analysis of zircon, Fe-Cr-Zn oxide particle in the matrix.
Fig. 10 – SEM micrograph of matt glaze containing 1 wt% raw ash and EDS analysis of zircon, Fe-Cr- Zn oxide particle in the matrix

Fig. 11 – SEM micrograph of transparent glaze containing 1 wt% raw ash and EDS analysis of zircon, Fe-Cr- Zn oxide particle in the matrix
form the zinc iron chromite brown spinel crystal structure\textsuperscript{25}. The EDS patterns revealed homogenous patterns that were similar in each of the experimental compositions. From the EDS spectra it is possible to observe zircon (Figs12 and 13) and small white crystals rich in Fe, Cr and Zn, typical composition of zinc iron chromite spinel, are evident. This is the new phase formed by the ferrochromium ash contribution into the glazes and it is responsible of the color development in these glazes.

Fig. 12 – SEM micrograph of opaque glaze containing 4 wt% of fly ash calcined at 1000°C and EDS analysis of selected areas and spot
Conclusions

The obtained results demonstrated that the ferrochromium fly ash pigment is chemically stable in the wall tile glazes at the studied calcination temperatures. In this study, it has been dedicated that the ferrochromium fly ash could be used as a coloring agent for brown colored products in ceramic tile manufacturing due to its ingredients, fine particle size distribution and brown color formation after heat treatments. The usage of these wastes as raw materials will contribute economical benefits for dye, pigment industry and ceramic tile industry. By analyzing the colorimetric parameters of wall tile glaze compositions colored by fly ash, it has been observed that effective factors were glaze type and amount of fly ash due to including of the new phase (zinc iron chromite brown spinel) and Fe$_2$O$_3$-Cr$_2$O$_3$ amount, respectively. But, the calcination temperature is not effective a factor on color formation. Controlling these main factors will provide intended color generation at glazed surfaces. To identify the main factors and levels affecting the production, by using less material, labor and time it has obviously seen that the factorial design of experiment is very conducive method.

References

19 http://www.faqs.org/patents/app/20100316560