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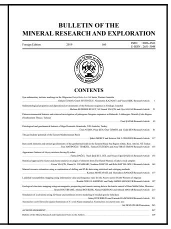

Appearance features of clayey mixtures having fly ashes

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Research Article

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ABSTRACT

The use of wastes has become very significant and widespread in terms of sustainable production of clayey mixtures, since the wastes provide many advantages. In this study, the effects of two different types of fly ash, which were wastes of Seyitomer and Cayirhan thermal power plants, on the color change of brick samples with various amount of fly ash ranging between 0 to 60% at different sintering temperatures were investigated. As a result, traditional red colored bricks could be produced with fly ash without using a separate raw material to meet the color requirements. It was found that desired colors for special architectural applications could also be achieved by using fly ash.

1. Introduction

Clay minerals are found in different forms in nature, they are divided into various classes according to their mineralogical properties, crystal structures, chemical contents, areas of use and physical properties.

The most known products of ceramics, one of the main uses of clays, are bricks, pottery, tiles and porcelain (Semiz, 2017). Ceramic products firstly emerged in Anatolia 8000 years ago. These products that became a part of human life at a certain stage of civilization are used in many areas such as architectural elements, decoration material and kitchen ware. Ceramic products can be considered as almost entirely domestic goods, so it is important to create added value in Turkey. Turkey is the sixth producer of ceramic tiles in the World and the third producer of ceramic tiles in Europe as a producer of ceramic tiles (TCF, 2018).

Color plays an active role in defining the properties and visual characteristics of materials (Ware, 2013). Therefore, the color difference is a physical quality parameter that is used in many fields from health sector to the food sector, from food to material science. This parameter can be measured by simple devices or even with visual inspection. Colorimeters have two chromatic coordinates that are red-green and yellow-blue and lightness channels. These devices also include glass filters derived from the characteristics of a standard human observer (Ware, 2013).

Fly ash and bottom ash are the primary products of coal burning process called as Coal Combustion Products (CCPs) and have been used as raw materials in various applications for about 80 years (Heidrich et al., 2013). Firing coal at thermal power plants' furnace over 1000 ° C results in the formation of fly ash by electrostatic filters or mechanical precipitation of the particles formed from the flue gases (ECOBA, 2010).

Studies for reuse of fly ash to produce materials such as bricks, ceramics, cement, concrete, glass, lightweight aggregates are still in progress all around the world (Eliche-Quesada et al., 2017). Karaman et al. (2006) were found that there was a negative relationship between the compressive strength and color measurement parameters of bricks (lightness

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and chromaticity coordinates). The relationship between the compressive strength and lightness, chromaticity coordinate of yellow-blue could be defined as linear regression equations. On the other hand, the relationship between the compressive strength and chromaticity coordinate of red-green was weak. Eliche-Quesada et al. (2017) found out that the mechanical properties of conventional clay bricks and bricks contained 20% of fly ash which were sintered at 1000°C were quite similar. According to Kockal (2012*a, b*), it was found that the shrinkage, water absorption and strength properties of commercial ceramic tiles were close to those obtained with fly ash substitution in the ceramic mixture. Kockal (2015) determined that at sintering temperature of 1130°C, the addition of fly ash to ceramic tiles resulted in reduced water absorption and increased shrinkage and strength. At 1210°C, compressive strength and shrinkage decreased and water absorption increased.

According to Turkish Statistical Institute (TUIK)'s data in 2016, total of 19.5 million tonnes of waste was generated in thermal power plants, of which 87.8% were ash and slag waste. While 83.3% of the total waste was disposed, only a small amount such as 16.7% was sent to waste recovery plants and mines (TUIK, 2018). For this reason, the aim of this study is to investigate the color changes of the clayey mixtures substituted by fly ash to be used to produce ceramic materials. In the study, two different fly ashes of Cayirhan and Seyitomer thermal power plants were used at different ratios and the mixtures were exposed to sintering at different temperatures. The color changes of these mixtures were measured by chroma meter and lightness factor and chromaticity coordinates of the samples were obtained and color differences were calculated. As well as, the experimental results were compared and discussed.

2. Materials and Methods

2.1. Materials

Chemical compositions of all raw materials are given in table 1. The clay was obtained from the Elmalı region of Antalya, Turkey. Fly ashes were obtained from Seyitömer (SFA) and Çayırhan (CFA) thermal power plants respectively located in Kütahya and Ankara, Turkey. Clay was replaced with both of the fly ashes at different percentages by weight. Moreover, tap water was used as a constituent of brick samples to give suitable shape to the samples.

2.2. Preparation of Brick Samples

In the study to obtain brick samples, six different mixtures (clay + fly ash) were prepared, in the amount of fly ash ranging between 0 and 60% by weight in 10% intervals. These mixtures were prepared identically for both types of the fly ashes (CFA and SFA). Homogenous mixtures were obtained by mixing with the addition of nearly 0.5 gram of water for each mixture.

In order to carry out the experiments, samples were produced in the shape of a cylinder. Samples with a diameter of 20 mm and a height of between 20 to 27 mm were prepared in order to obtain aspect ratio (d/h) of nearly 1. The total amounts of the mixtures were set at the optimum amounts to keep the height of these samples between the specified values. The mass values of the mixtures was determined separately for each percentage of fly ash through trial and error; the mass of samples containing 0% fly ash was 18 grams (water + clay) and 60% fly ash (water + clay + fly ash) was 14 grams. Cylinder samples were molded with a hydraulic press of 15 tonnes under 110 bar pressure and 10 seconds of time for each percentage of fly ash.

After pressing, the fresh samples were dried at 80°C to obtain constant mass for about 2 h. Then, the oven dried fresh samples were sintered at three different temperatures that were 850,950 and 1050°C in a muffle furnace. The sintered samples are coded as shown in table 2. Loss on ignition values of all sintered samples are given in figure 1, 2. In this table and figures "S" represents SFA and "C" represents CFA.

Table 1- Chemical compositions of raw materials.

Raw Materials	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_20	CaO	TiO_2	Cr_2O_3	MnO	Fe_2O_3
SFA	0.66	3.65	24.89	51.04	0.08	0.32	2.31	3.12	0.90	0.10	0.12	11.79
CFA	9.18	8.29	13.11	34.90	0.72	2.81	2.68	21.93	0.51	<0.0007	0.08	5.43
Clay	0.57	8.12	15.04	34.13	0.35	0.08	2.13	27.95	0.70	0.11	0.13	10.11

Table 2- Codes of brick samples.

Sintering Temperature (°C)	Fly Ash Content of Brick Samples (%)						
	0	10	20	30	40	50	60
850	K-850	10 S-850/ 10 C-850	20 S-850/ 20 C-850	30 S-850/ 30 C-850	40 S-850/ 40 C-850	50 S-850/ 50 C-850	60 S-850/ 60 C-850
950	K-950	10 S-950/ 10 C-950	20 S-950/ 20 C-950	30 S-950/ 30 C-950	40 S-950/ 40 C-950	50 S-950/ 50 C-950	60 S-950/ 60 C-950
1050	K-1050	10 S-1050/ 10 C-1050	20 S-1050/ 20 C-1050	30 S-1050/ 30 C-1050	40 S-1050/ 40 C-1050	50 S-1050/ 50 C-1050	60 S-1050/ 60 C-1050

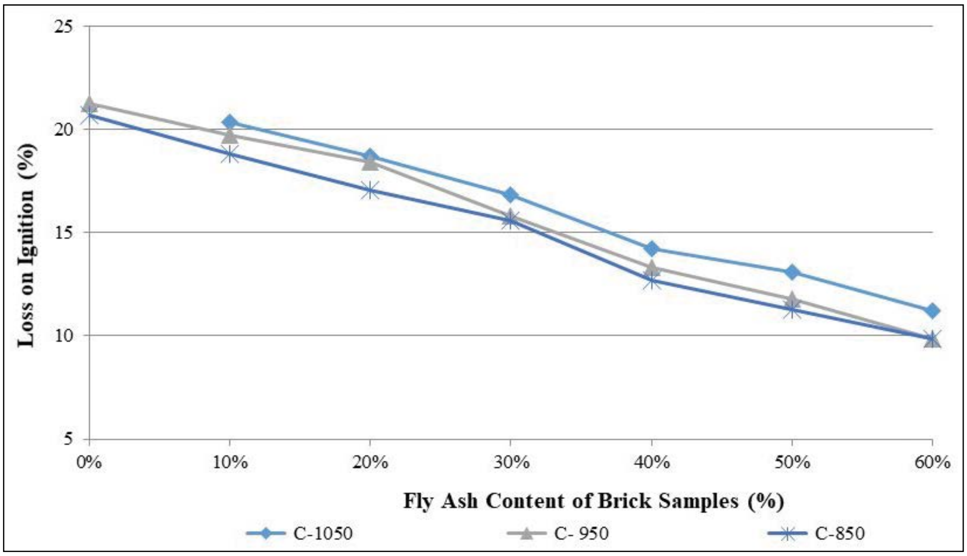

Figure 1- Loss on Ignition versus Fly Ash Content of Brick Samples containing CFA.

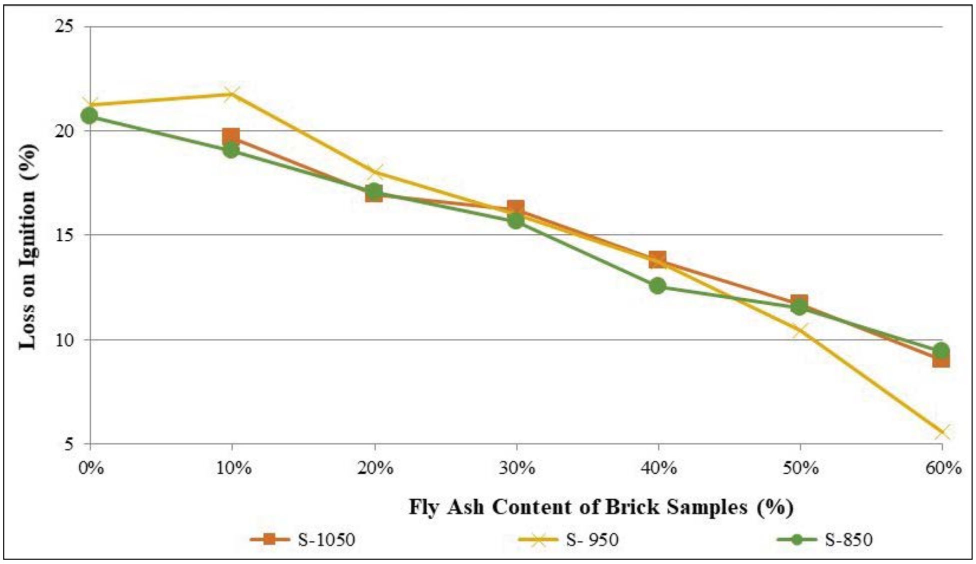

Figure 2- Loss on Ignition versus Fly Ash Content of Brick Samples containing SFA.

2.3. Experimental Methods

The chemical analyses of the raw materials were carried out by X-Ray Fluorescence (XRF). Loss on ignition values of all sintered samples were calculated by the equation below:

$$\mathbf{LOI} = \frac{W_f - W_s}{W_f} \times \mathbf{100} \qquad (1)$$

where W_f is the weight of oven-dried fresh samples and W_s is the weight of sintered samples.

The sintered samples were measured with the FRU Chroma Meter colorimetrically. The color difference (E) was calculated by the following equation with the sample's lightness factor (L) and chromaticity in other words chromaticity coordinates a (red) and b (yellow):

$$\Delta \mathbf{E} = \sqrt{\Delta \mathbf{L}^2 + \Delta \mathbf{a}^2 + \Delta \mathbf{b}^2} \quad (2)$$

3. Results and Discussion

In terms of the production of sustainable ceramic products, the wastes such as fly ash could be used to replace flux agents. These agents are generally alkaline and alkali oxides (K_2O, Na_2O, MgO, CaO) of the raw material that allow proper sintering at low temperatures. In addition, these wastes control the plasticity and shrinkage of the ceramics and so enable us to save raw materials and energy (Sultana et al., 2015; Kockal, 2012*b*).

Actually because of this, the color variations of the clay mixtures with substitution of different types of fly ashes were examined. Furthermore, the effects of sintering temperature, fly ash content and type on color change and lightness factors were investigated.

The results obtained from the measurements of chroma meter on the sintered samples were as indicated in table 3. The results given are the average of the measurements. During the sintering process at 1050°C, control samples lost their structural integrity. Therefore, the pronounced samples were not measured.

Table 3- Color measurement results of the brick samples.

	K-1050	**10 S-1050**	**20 S-1050**	**30 S-1050**	**40 S-1050**	**50 S-1050**	**60 S-1050**
L	--	64.23	62.09	57.58	54.79	52.84	51.09
a	--	9.77	10.34	11.61	12.24	12.98	13.67
b	--	22.90	21.76	20.65	19.45	18.70	18.49
E	--	68.88	66.60	62.26	59.42	57.53	56.02
	K-1050	**10 C-1050**	**20 C-1050**	**30 C-1050**	**40 C-1050**	**50 C-1050**	**60 C-1050**
L	--	67.62	69.36	69.67	69.91	69.95	69.27
a	--	8.17	6.12	5.47	4.97	4.61	4.64
b	--	22.81	22.20	21.48	20.88	20.21	19.19
E	--	71.82	73.08	73.11	73.13	72.95	72.02
	K-950	**10 S-950**	**20 S-950**	**30 S-950**	**40 S-950**	**50 S-950**	**60 S-950**
L	66.12	65.07	62.97	62.16	59.96	59.29	57.69
a	9.65	10.14	10.92	11.56	12.79	13.90	13.91
b	23.54	22.84	22.32	22.09	22.89	24.43	23.21
E	70.85	69.70	67.69	66.97	65.45	65.62	63.72
	K-950	**10 C-950**	**20 C-950**	**30 C-950**	**40 C-950**	**50 C-950**	**60 C-950**
L	66.12	65.97	65.57	65.72	65.32	64.48	64.88
a	9.65	8.65	8.35	7.85	7.62	7.35	7.06
b	23.54	21.79	20.68	19.18	18.19	17.22	16.17
E	70.85	70.01	69.26	68.90	68.23	67.14	67.23
	K-850	**10 S-850**	**20 S-850**	**30 S-850**	**40 S-850**	**50 S-850**	**60 S-850**
L	63.60	62.67	62.14	62.05	62.12	61.73	61.33
a	10.13	10.01	10.37	10.58	10.76	10.74	10.98
b	22.20	21.48	22.04	21.91	22.02	21.35	21.49
E	68.12	67.00	66.74	66.65	66.77	66.19	65.91
	K-850	**10 C-850**	**20 C-850**	**30 C-850**	**40 C-850**	**50 C-850**	**60 C-850**
L	63.60	63.65	63.72	63.38	62.51	62.57	62.15
a	10.13	9.36	8.64	8.22	7.69	7.56	7.15
b	22.20	20.93	19.77	18.60	17.17	16.70	15.30
E	68.12	67.65	67.27	66.56	65.28	65.20	64.40

For SFA-containing brick samples, there was an inverse relationship between the fly ash content and lightness factor (L) at all sintering temperatures.

Considering the lightness factor in CFA-containing brick samples, it was observed that there was a slight fluctuation differently from the samples with SFA. The rise in the lightness factor of brick samples is due to the decline in the amount of Fe_2O_3 and organic materials (Kockal, 2012*a*). Thus, the increment in the lightness factor of SFA-containing brick samples was based on extreme Fe_2O_3 content even higher than the clay as seen in table 1. Besides, almost constant L values of CFA-containing brick samples could be attributed to the balancing effect of low Fe_2O_3 content and loss on ignition values. Chromaticity coordinates (a and b), which were another criteria of color change, gave dissimilar results for SFA and CFA containing samples. Foremost, it was seen that red color (a) increased and yellow color (b) decreased in brick samples containing SFA at 1050°C. In fact, this situation could be visible in figure 3a. Furthermore, there was reduction between 10C-1050 to 60C-1050 for both of red and yellow colors by 43% and 16% respectively, as could be noticed roughly in figure 3b.

The color of ceramic products can vary from light red to dark brown depending on rise of the amount of Fe_2O_3. In order to obtain glazed or unglazed white ceramic products, the amount of Fe_2O_3 should be in the range of 1-2% (Dondi et al., 2014). Because the Fe_2O_3 content of the SFA was as high as about 12%, the red color became darker for 60S-1050. On the other hand, since the content of Fe_2O_3 of CFA was lower than clay and the content of CaO (which has white color) was quite higher than SFA and nearly the same with clay, CFA-contained samples' color experienced lightening at large ratios.

Taking the results of 950°C into consideration, it was recognized that the brick samples containing SFA and K-950 showed stagnate trend for the chromaticity coordinates of yellow (Figure 4a) but the red color trend nearly was the same as it was at 1050°C. In addition to this, CFA-containing brick samples displayed decrement on the chromaticity coordinates of red and yellow (Figure 4b). It was identified that the color changes due to the amount of fly ash demonstrated nearly stable state for both types of fly ash at the sintering temperature of 950 °C. At the sintering temperature of 850°C, the deviation of the chromaticity coordinates of red between K-850 and 60S-850 was only 8%. The chromaticity coordinates of yellow of K-850 and 60S-850 changed slightly with a value of 3% reduction (Figure 5a).

These results suggest that there was almost no change in the colors of brick samples with the

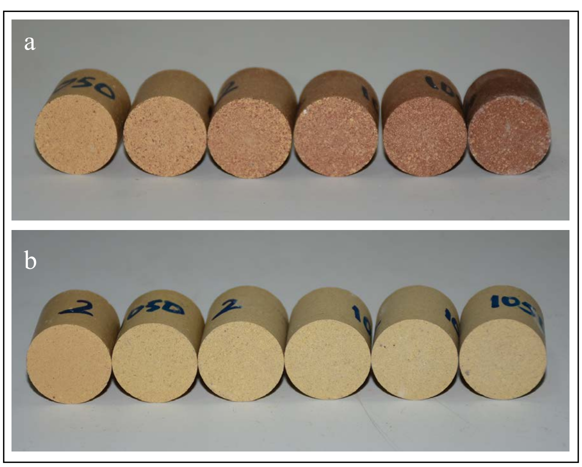

Figure 3- a*) SFA-containing brick samples sintered at 1050°C **The figure shows the brick samples containing 10% fly ash on the left hand and 60% fly ash on the right hand, so the fly ash content increases from left to the right.*
b*) CFA-containing brick samples sintered at 1050 ˚C **The figure shows the brick samples containing 10% fly ash on the left hand and 60% fly ash on the right hand, so the fly ash content increases from left to the right.*

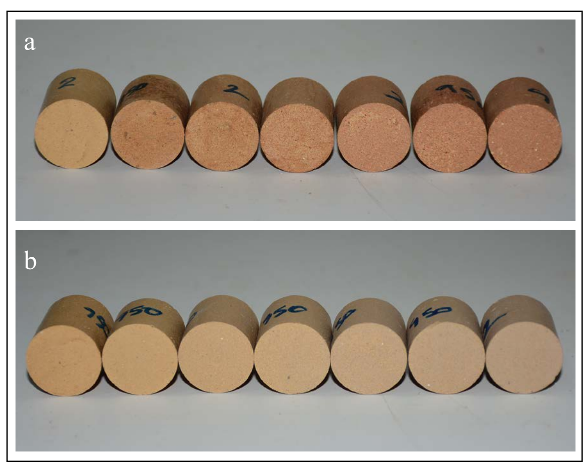

Figure 4- a*) SFA-containing brick samples sintered at 950°C **The figure shows the brick samples containing 0% fly ash on theleft hand and 60% fly ash on the right hand, so the fly ash content increases from left to the right.*
b*) CFA-containing brick samples sintered at 950°C **The figure shows the brick samples containing 0% fly ash on the left hand and 60% fly ash on the right hand, so the fly ash content increases from left to the right.*

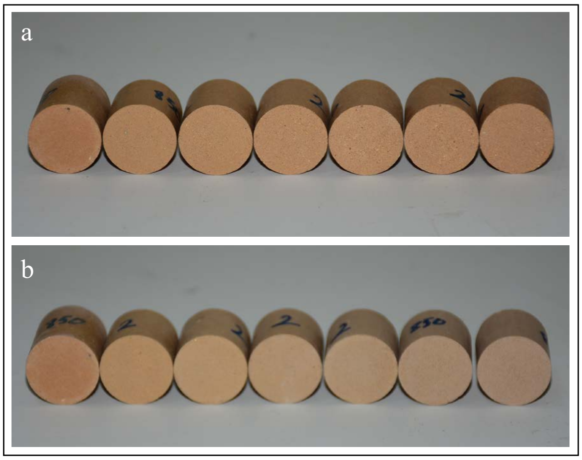

Figure 5- a*) SFA-containing brick samples sintered at 850°C**The figure shows the brick samples containing 0% fly ash on the left hand and 60% fly ash on the right hand, so the fly ash content increases from left to the right.*
b*) SFA-containing brick samples sintered at 850°C**The figure shows the brick samples containing 0% fly ash on the left hand and 60% fly ash on the right hand, so the fly ash content increases from left to the right.*

variation of fly ash content at the sintering temperature of 850°C. The chromaticity coordinates of red and yellow lessened at a nearly close rate of 30%, as K-850 compared with 60C-850 (Figure 5b).

It was seen that the general tendency was in the direction of cutting down the color difference with the rise of the fly ash ratio for all brick samples. It was noted that lightness (L) and color difference fell off with a rise of the sintering temperature 850 to 1050 for the samples coded as 40 S, 50 S and 60 S at the constant fly ash content. The amount of this decrement was found to be at most for 60 S-coded samples. 60 S-950 reduced in lightness by 5.9% and color difference by 3.3%; 60 S-1050 declined in lightness by 16.7% and color difference by 15% compared to 60 S-850 (Figure 6).

Figure 6- Brick samples containing 60% SFA (constant ratio) sintered at different temperatures.

As well as, for all brick samples containing SFA, the chromaticity coordinate of red was directly related to the content of fly ash and the sintering temperature, but yellow color was inversely proportioned.

It was stated that the liquid phase formed by increasing the sintering temperature decreased the porosity. As a result of this, the crack formation was minimized and mechanical behaviours such as bending strength developed (Celik, 2010).

It was observed that SFA containing samples with a constant content of fly ash, despite including the same amount of Fe_2O_3, the red color increased and the lightness decreased thanks to the liquid phase formation at high sintering temperature. Lastly, the evaluation was performed for CFA-containing brick samples with respect to sintering temperatures. It was detected that the chromaticity coordinates of red had decrement and reversely, yellow color had increment (Figure 7).

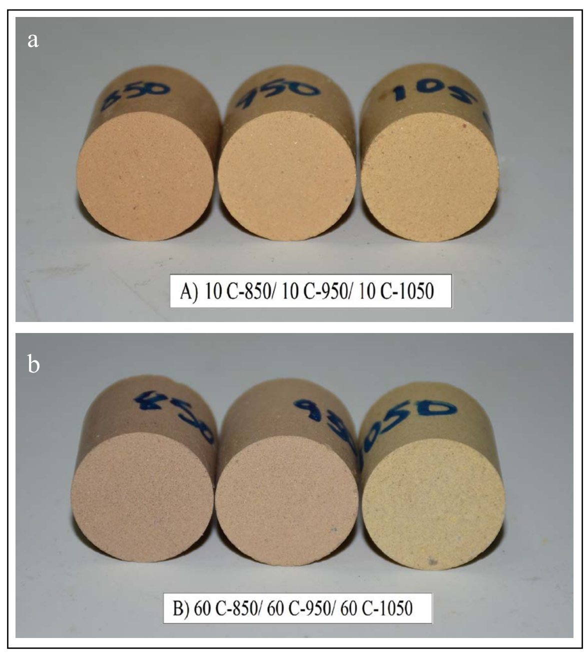

Figure 7- a) Brick samples containing 10% CFA (constant ratio) sintered at different temperatures. b) Brick samples containing 60% CFA (constant ratio) sintered at different temperatures.

4. Conclusions

Some reasonable conclusions were obtained according to experimental studies.

- ➢ As the fly ash ratio and the sintering temperature increased the red color coordinate decreased for CFA-containing samples and increased for the SFA-containing samples. In other words, both of two fly ash types led to different colors for the brick samples.

- ➢ The clay used in the experiment is also the raw material of the brick producers and another clay type is practically used to provide the red color in the industry to meet ordinary request of the consumers. Thus, this study resulted in the use of fly ash, a waste, instead of the secondary raw material. Nevertheless, by consumption of fly ash, saving the secondary raw material and energy will be achieved.

- ➢ Especially SFA, which caused significant increase in red color, promises hope for conventional brick production.

- ➢ Moreover, in some architectural applications, different colors are desired. It was inferred that different types and contents of fly ash could be used to meet this requirement in the brick production. This situation will ensure that there is no need for additional glazing and painting operations for these specific applications.

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References

Celik, H. 2010. Technological characterization and industrial application of two Turkish clays for the ceramic industry. Applied Clay Science, 50(2), 245-254.

Dondi, M., Raimondo, M., Zanelli, C. 2014. Clays and Bodies For Ceramic Tiles: Reappraisal and Technological Classification. Applied Clay Science, 96, 91-109.

Eliche-Quesada, D., Sandalio-Pérez, J. A., Martínez-Martínez, S., Pérez-Villarejo, L., Sánchez-Soto, P. J. 2017. Investigation of use of coal fly ash in eco-friendly construction materials: fired clay bricks and silica-calcareous non fired bricks. Ceramics International, 44(4), 4400-4412.

ECOBA (European Coal Combustion Products Association) 2010 Statistics. http://www.ecoba.com/ecobaccpprod.html. April 25, 2018.

Heidrich, C., Feuerborn, H. J., Weir, A. 2013. Coal combustion products: a global perspective. World of Coal Ash Conference 22-25 April 2013, Kentucky, 22-25.

Karaman, S., Gunal, H., Ersahin, S. 2006. Assesment of clay bricks compressive strength using quantitative values of colour components. Construction and Building Materials, 20(5), 348-354.

Kockal, N. U. 2012*a*. Properties and microstructure of porous ceramic bodies containing fly ash. Journal of building physics, 35(4), 338-352.

Kockal, N. U. 2012*b*. Utilisation of different types of coal fly ash in the production of ceramic tiles. Boletín de la Sociedad Española de Cerámica y Vidrio, 51(5), 297-304.

Kockal, N. U. 2015. Optimizing Production Parameters of Ceramic Tiles Incorporating Fly Ash Using Response Surface Methodology. Ceramics International, 41(10), 14529-14536.

Semiz, B. 2017. Characteristics of clay-rich raw materials for ceramic applications in Denizli region (Western Anatolia). Applied Clay Science, 137, 83-93.

Sultana, M. S., Ahmed, A. N., Zaman, M. N., Rahman, M. A., Biswas, P. K., Nandy, P. K. 2015. Utilization of hard rock dust with red clay to produce roof tiles. Journal of Asian Ceramic Societies, 3(1), 22-26.

TCF (Turkish Ceramic Federation). 2018. http://www.serfed. com/tr/content.php?content_id=125. April 25.

TUIK (Turkish Statistical Institute). 2018. Thermal Power Plant Water, Wastewater and Waste Statistics. http://tuik.gov.tr/PreHaberBultenleri.do?id=24873. April 23.

Ware, C. 2013. Information Visualization: Perception for Design, Elsevier, 513 p.