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Development of ceramic tiles from coal fly ash and tincal ore waste

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Abstract

The effect of coal fly ash and borax solid waste (TW) on the properties of wall tile was investigated. The properties examined include firing strength, firing shrinkage, water absorption and microstructure. A number of wall tile compositions were prepared by the replacement of potassium feldspar with the fly ash and TW in the range of 2–10%. Further on, the wall tiles were produced by replacing potassium feldspar (in the presence of fixed quantity of 2% TW and 5% TW) with the fly ash in the range of 2–10%. The results showed that firing strength of the wall tile increased when the fly ash and TW used in the preparation of the standard tile composition. In particular, the improvement of strength was observed when the TW up to 6 wt.% was introduced as potassium feldspar replacement. Results indicate an interesting potential for the coal fly ash and TW recycling to produce useful materials.

Keywords: Coal fly ash; Wall tile; Firing strength; Water absorption; Borax solid waste

1. Introduction

The recycling of by-products and wastes represents an increasingly urgent problem for the immediate future of human kind. Two major by-products are coal fly ash and boron waste, which are produced in significant amounts in Turkey. Of the two wastes, currently, only a small percentage of fly ash is utilized, the remaining being directly discharged into landfill, which is unsatisfactory solution both from ecological and economic point of view. Therefore, there is continuing interest in establishing suitable processes in which they can be efficiently reused.

The major constituents of fly ash are SiO_2, Al_2O_3 and Fe_2O_3 with some minor constituents such as CaO, MgO and other oxides. Therefore, these oxides have been mainly considered as a low cost material resource for the cement industry [1,2]. The fly ash is also used in the manufacturing of brick [3], fly ash mineral-based polymer composites [4] ceramic tableware and artware [5]. Recent studies have showed and alternative ways of the management of coal fly ash in using in glass [6] and glass-ceramics industry [7,8].

Boron wastes mainly are generated from the boron recovery system. Tincal waste is usually a valuable source of minerals containing SiO_2, B_2O_3, CaO, MgO and other oxides. Recently, it has been proposed as recycled raw material for the production of cement [9]. But, there has not been done much research on the use of tincal waste for ceramic production. According to Sheng [10], coal fly ash with large amounts of glass network formers ($SiO_2 + Al_2O_3$) can be used to obtain durable product and it is a promising material for use in the immobilization of borate waste. In this study, an attempt has been made to test the possibility of recycling fly ash and tincal waste in ceramic production. Several tile compositions have been formulated using varying proportions of the tincal waste and fly ash. The tailings have been characterized with respect to their chemical composition, mineral phase presents, etc.

2. Experimental

2.1. Materials and processing

The raw materials used in the present study are coal fly ash coming from the Seyitömer thermal plant (Kütahya,

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Table 1
Chemical analysis of raw materials (wt. %)

Item	Clay (A)	Clay (B)	Clay (C)	Potassium feldspar	Sodium feldspar	Quartz	Dolomite	Fly ash	Tincal waste
SiO_2	51.3	47.5	62.3	73.6	67.7	90.8	–	51.3	17.1
Al_2O_3	29.4	32.2	23.1	15.4	20.5	4.8	–	19.7	2.6
Fe_2O_3	2.6	2.9	1.8	0.4	0.3	0.4	0.04	10.7	0.4
CaO	0.6	0.4	0.5	1.1	1.3	0.1	30.8	4.8	16.9
MgO	0.7	0.5	0.3	0.1	0.3	0.1	22.6	3.2	15.4
Na_2O	0.2	0.1	0.7	3.3	8.0	0.2	–	0.8	2.9
K_2O	2.7	2.0	2.9	5.0	0.7	1.1	–	2.7	1.1
B_2O_3	–	–	–	–	–	–	–	–	11.0
TiO_2	1.4	1.4	1.4	0.4	0.5	0.5	–	1.2	0.03
Loss on ignition	10.5	12.8	6.8	0.8	0.6	1.9	46.1	2.1	28.9

Turkey), tincal waste from Etibank Boron Plant (Kırka-Eskişehir, Turkey), industrial feldspar, clay, quartz, and dolomite. Tincal waste used is a crude native borax. The chemical compositions of the raw materials are given in Table 1. Four series of batches and one reference mixture have been prepared. Standard batch composition used as a reference consisted of 47 wt.% kaolonitic clay minerals, 25 wt.% potassium feldspar, 10 wt.% sodium feldspar, 14 wt.% quartz, 4 wt.% other additives and designated "R". Potassium feldspar was replaced with increasing amount of fly ash and TW. The details of the batches composition are given in Table 2. Every batch was wet milled with a dispersing agent for 5 h. Milled slurries were passed through a 150 μm sieve and then dewatered. The filter cakes that formed were oven-dried for 2 days at 110 °C and then were ground to produce a fine powder. Bodies of 100 mm × 100 mm × 6 mm were obtained by cold axial pressing at 40 MPa. The samples were fired in refractory roller furnace for 34 min at 1020 °C.

2.2. Properties characterization

The drying shrinkage, firing shrinkage, water absorption and firing strength were determined for each specimens

Table 2
Batch composition (wt.%)

	R[a]	F_1	F_2	F_3	F_4	F_5	T_1	T_2	T_3	T_4	T_5	M_1	M_2	M_3	M_4	M_5	K_1	K_2	K_3	K_4	K_5
Potassium feldspar	25	23	21	19	17	15	23	21	19	17	15	23	21	19	17	15	21	19	17	15	13
Tincal waste	–	–	–	–	–	–	2	4	6	8	10	5	5	5	5	5	2	2	2	2	2
Fly ash	–	2	4	6	8	10	–	–	–	–	–	2	4	6	8	10	2	4	6	8	10

[a] Clay (A) = 18, clay (B) = 12, clay (C) = 17, sand = 14, sodium feldspar = 10, dolomite = 4.

Table 3
Properties of materials obtained

Sample	Water absorption (%)	Los on ignition (%)	Drying shrinkage (%)	Firing shrinkage (%)	Modulus of rupture (N/mm^2)
R	13.17	7.58	0.050	2.53	9.0
F_1	13.65	6.92	0.062	3.07	11.7
F_2	12.93	7.44	0.062	3.28	11.8
F_3	12.82	7.54	0.060	3.45	12.5
F_4	13.13	7.53	0.050	3.56	13.0
F_5	13.44	7.59	0.050	3.85	15.1
T_1	10.93	7.75	0.010	3.23	18.0
T_2	8.87	8.22	0.056	4.82	23.5
T_3	7.31	8.86	0.044	6.21	30.2
T_4	6.23	9.44	0.037	6.36	24.5
T_5	7.52	9.92	0.074	5.23	18.0
M_1	8.62	8.39	0.112	5.31	23.4
M_2	8.35	8.56	0.075	5.31	24.1
M_3	8.31	8.38	0.050	5.51	26.0
M_4	8.21	8.56	0.031	6.10	26.2
M_5	7.54	8.54	0.050	6.14	27.0
K_1	12.43	7.10	0.024	2.25	18.8
K_2	12.74	7.03	0.020	2.53	18.5
K_3	12.41	7.16	0.020	2.89	18.4
K_4	11.72	7.20	0.019	3.33	18.4
K_5	11.51	7.25	0.020	3.35	18.9

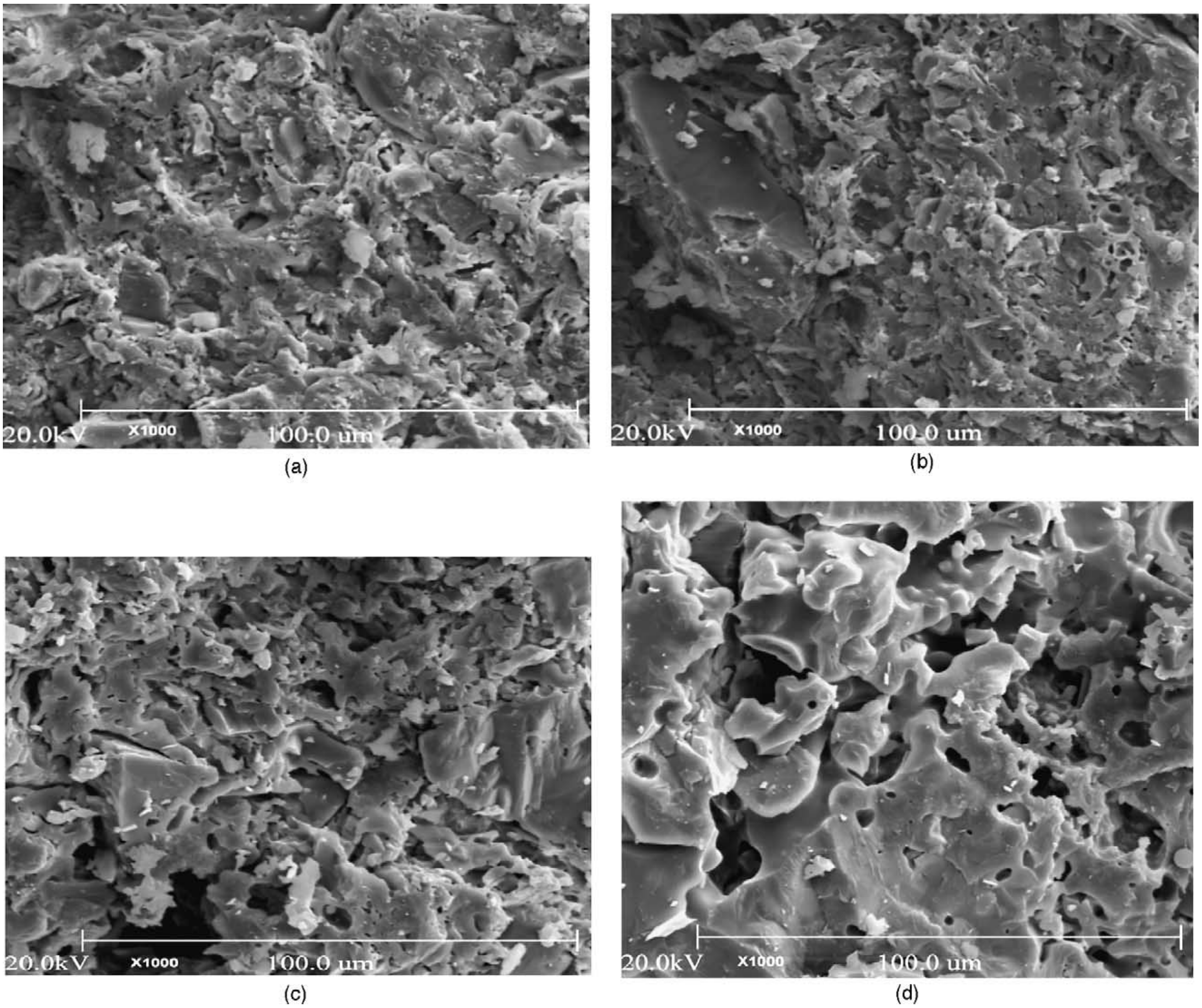

Fig. 1. (a) SEM of fractured surface of R tiles fired at 1020 °C. (b) SEM of fractured surface of F_1 tiles fired at 1020 °C. (c) SEM of fractured surface of T_1 tiles fired at 1020 °C. (d) SEM of fractured surface of M_1 tiles fired at 1020 °C.

according to TS EN ISO 10545 [11]. The phases present in the samples were characterized by X-ray difractometry (SHIMADZU XRD-6000). The microstructure of the fractured surface of sintered specimens was examined by SEM (Jeol JXA 840A). Differential thermal analysis (DTA) scans of specimens were carried out by a NETZCH Thermal analyzer (STA 409 EP). Tests were performed on powdered samples at a heating rate of 10 °C min^{-1} from room temperature to 1100 °C, in a platinum crucible, with calcined alumina as reference.

3. Results and discussion

Various physical and mechanical properties of wall tile bodies obtained from fly ash and TW were listed in Table 3. The Firing strength results shown Table 3 reveal that regardless of replacement level, TW and fly ash increased the strength of the tile, as compared to that of the control specimen. The rate of increase in the strength of the tile is higher when the amount of the TW and fly ash content increases. Although this study does not contain a quantitative phase analysis, it has been suggested that the strength development with increasing fly ash content is directly related to the mullite content of the fired sample [12]. It is worth mentioning that TW is more effective than fly ash in terms of increasing the firing strength. This difference in firing strength of the specimens may be attributed to the high content of Na_2O and B_2O_3 in TW, which results in an increased rate of sintering and leads to an improvement in the extend of interaction among particles. Adding TW in the tile composition increases the strength in T_1, T_2, T_3, whereas in the case of T_4 and T_5 the firing strength decreases. This may be due to fact that the potassium feldspar has been replaced by the TW, and the compositions contain progressively much of B_2O_3, which results in the formation of undesired level of glass phase causing a reduction in the firing strength of the bodies.

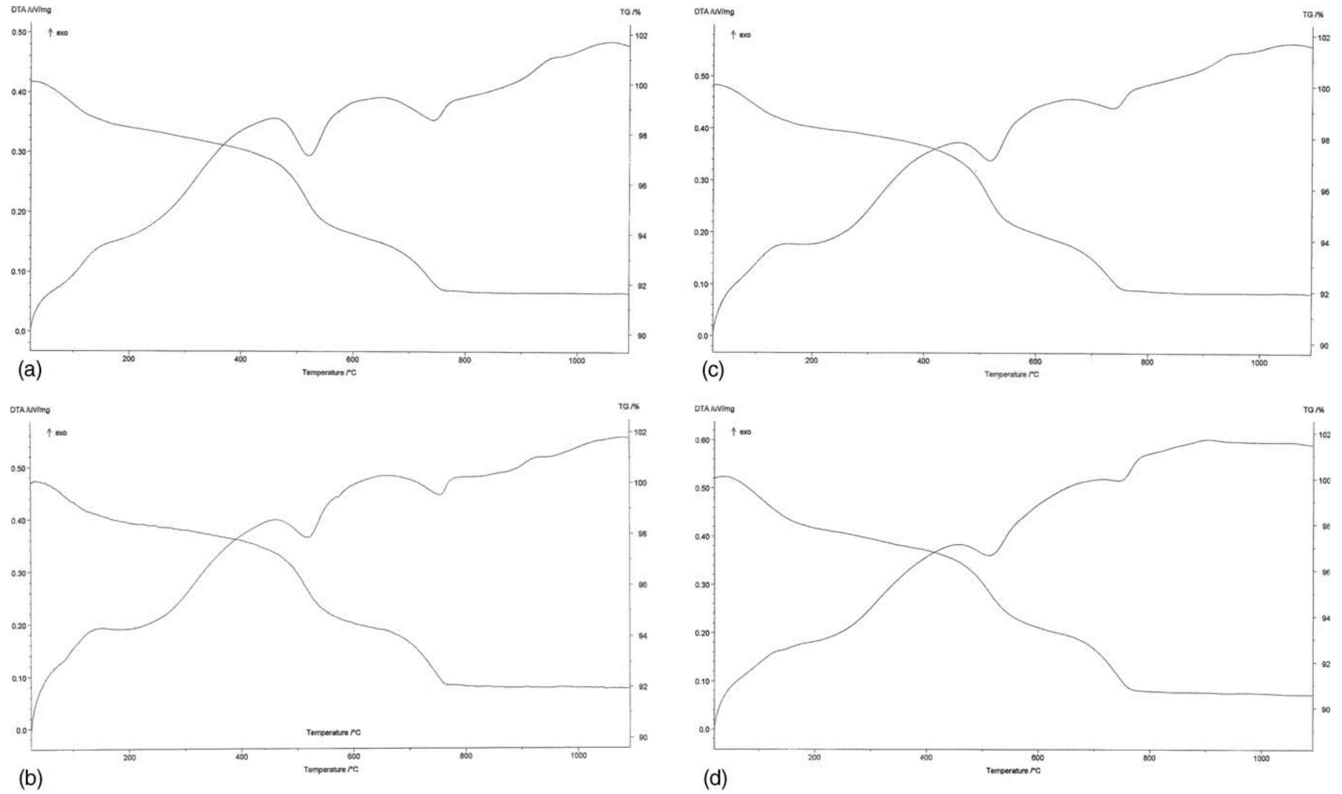

Fig. 2. (a) DTA and TG plots of the tile R. (b) DTA and TG plots of the tile T_1. (c) DTA and TG plots of the tile F_1. (d) DTA and TG plots of the tile M_1.

The firing strength results from Table 3 also show that regardless of replacement level of fly ash, the incorporation of 2–10% fly ash with 5% TW results in a significant increase in the strength of the specimens compared to the strength of the tile containing fly ash. However, a gradual loss in the strength of tiles was observed with decreasing TW content compared to specimens (containing, 2–10% of fly, and 5% of TW). This may be explained by the B_2O_3, Al_2O_3 + SiO_2 content of the TW and fly ash, respectively. The Al_2O_3 and SiO_2 are known as network formers, and the

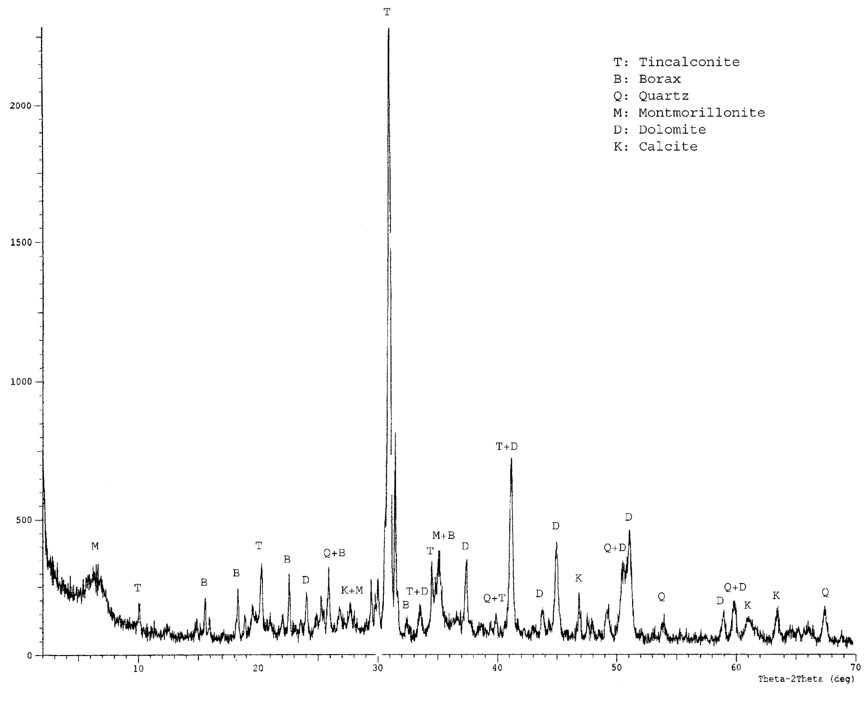

Fig. 3. XRD pattern of tincal concentrator waste.

addition of TW to the system increases the network former capacity of it, and results in a further strengthening of the tile compared to control specimens. According to this the use of both fly ash and TW together gives an opportunity of controlling strength of the tiles.

Table 3 includes firing shrinkage of the tiles in relation to fly ash and TW content. The values of firing shrinkage increased with the increase in fly ash content of the tile. The same tendency was also observed for specimens containing TW (except T_5). However, the firing shrinkage values for tiles containing fixed quantity of TW (5%) were higher than that of the control tile and the tile formed with substitution of 2–10% fly ash. When the replacement level of TW was reduced to 2%, the effect that they had on the shrinkage rise tended to be compensatory. Thus, the initial shrinkage gain provided by the high content of TW was offset by the reduced ratio of TW/fly ash content. It may be suggested that a high content of fluxing oxides, B_2O_3, Na_2O, K_2O in the system helps the formation of glassy phases which fill in the pores, thus leading to a shrinkage gain during to firing. The result also indicates that the combination of fly ash and TW gives the opportunity to balance the shrinkage gain resulted from high level of B_2O_3 content in TW.

Water absorption values of all prepared bodies are given in Table 3. Water absorption rate has been used as an indication for porosity of the tile body. The water absorption of the tile decreased with the increase of the fly ash and TW content. In comparison, tile containing fly ash had higher water absorption than that made from TW. At different TW/fly ash ratios, tiles with 5% substitution of TW had lower water absorption than the one containing 2% TW. These observations suggest that an increased rate of sintering resulted from B_2O_3 causes less pores in tile body.

The microstructures of the fractured surface of samples fired at 1020 °C are shown in Fig. 1(a–d). It was observed from the micrographs that crystalline materials were embedded in a glassy matrix and microstructures of the tile bodies were not thoroughly homogeneous. Compared to sample F_1 (containing 2% fly ash), the fracture surface of the control sample showed a more dense well-sintered microstructure with a uniform distribution of pores. It appears from Fig. 1c that the sample T_1 contain a greater number of grains than F_1 and the control sample. The fracture surface of the sample prepared from fly ash and TW (5% TW + 2% fly ash) was very different from the others with more dense well-sintered microstructure associated with the formation of elongated cavities. From these results, it may be suggested that this dense microstructure is responsible for better mechanical properties of the sample.

3.1. Thermal analysis

TG/DTA data of selected samples is shown in Fig. 2a–d. The mass loss graph clearly shows in which temperature ranges the loss on ignition (mass loss) is the greatest. Studies on other wastes have reported that a mass loss up to 250 °C results from the expulsion of remaining water and gasification of organic component [13]. A significant weight loss occurs between 400 and 770 °C. In the temperature range from 400 to 600 °C the water of crystallization is dissociated and around 740 °C the calcite decomposition occurs.

The DTA curves of the wall tile bodies containing waste display a good compatibility between this waste and the ceramic body. Inclusion of waste into the tile body lowers both endothermic peak at about 520 °C, and the exothermic peak at about 960 °C due to a possible mullite phase formation.

3.2. Mineralogical analysis

The X-ray diffraction patterns of the waste raw material under investigation are given in Fig. 3. In the TW the main constituent is Tincalconite ($Na_2B_4O_7{\cdot}5H_2O$), followed by Borax ($Na_2B_4O_7{\cdot}10H_2O$), quartz (SiO_2), montmorillonite, dolomite and calcite. These mineralogical data confirm that TW is mostly adequate for the mixing with the ceramic body.

4. Conclusions

In this study we demonstrated that it is possible to utilize fly ash and TW as alternative raw material resources for the production of the wall tile.

On the basis of the results reported in the present investigation, the following conclusion can be drawn:

1. The use of TW and fly ash in the standard wall tile composition increases the firing shrinkage. Moreover, combination of fly ash and TW enable to control firing shrinkage of the tile.
2. Regardless of the replacement level, introduction of fly ash and TW into wall tile composition increases the firing strength compared to that of standard wall tile. This increases in the firing strength is more pronounced as the replacement level of TW and fly ash content is increased.
3. Firing strength of the tiles containing TW is higher than that of the control tile and the tile containing fly ash. The result shows that the firing strength is directly related to the TW content in the wall tile, which increases as the TW content of the tile compositions is increased.
4. Water absorption of tile decreases as the TW content of the tile is increased.
5. Tiles containing up to 10 wt.% of fly ash of and 5 wt.% of TW into wall tile body show a good mineralogical and rheological compatibility with the pure wall tile product.

Despite these obvious benefits, two other main aspects should be considered: first, the mineralogical and chemical composition of fly ash and TW differ from one source to another. Hence, no general use can be applied in ceramic production. Second, TW sometimes contains a high amount of B_2O_3, which can represents a serious problem that may affect the tile, as to mention just the occurrence of undesirable levels of glassy phases.

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