

## The influence of coal bottom ash and tincal (boron mineral) additions on the physical and microstructures of ceramic bodies

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In this paper, the influence of coal bottom ash and tincal additions on the physical properties and microstructures of the standard wall tile body composition was investigated. Water absorption, firing strength, dry and fired shrinkage tests of the incorporated ceramic bodies and reference body were done. Microstructures of sintered tiles were analyzed using a scanning electron microscope (SEM). The results show that tincal additions to the ceramic body improved the physical properties of the tiles. As a result, tincal can be used as a flux material in the ceramic bodies due to its favorable effects on the water absorption and fired strength. The results revealed that bottom ash can be used in the ceramic tile body composition. When bottom ash was used in the ceramic industry, environmental hazards of bottom ash are inhibited. Furthermore, bottom ash is transformed to an economic product.

**Key words:** Bottom ash, Tincal, Tile, Strength, Microstructure, Ceramic, Body

### Introduction

Worldwide, Turkey, the USA and Russia have the most abundant boron mines. In terms of total reserve basis, Turkey has a share of 72.20% and the USA has 6.8% [1]. The main boron minerals in Turkey are tincal, colemanite and ulexite and the average boron ore production is in the range of approximately 1.3 million tons per year [2].

Tincal is a borax mineral ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ) which is transparent-white in color, has a monoclinic prism shape and has a density of 1.7. It is made up of 36.5%  $\text{B}_2\text{O}_3$ . Tincal is produced by the open pit mining method. It is a cheap and abundant material. Tincal ore is processed by wet methods which include classifying and sizing. Processed tincal is sold as a concentrate tincal. Borax pentahydrate is produced by using dissolution, filtration, crystallization, drying sieving methods from concentrate tincal in Turkey.

Borax is widely used as a flux for glazes on earthenware, art, and other types of ceramic bodies [3]. Borax is a strong alkaline flux that is mostly used in low-temperature ceramics. Because it is soluble, it is best to use borax in frit form-a chemically converted version that is stable and no longer soluble. The addition of small amounts of borax to a glaze will increase the smoothness of a glaze as it melts [4].

Bottom ash is a waste material that is discarded continuously from thermal power plants. Therefore, the

amount of bottom ash which is deposited near the power plant increases over time. Thus, bottom ash has serious effects on the environment. Coal bottom ash and boiler slag are coarse, granular, incombustible by-products. They are collected from the bottom of coal furnaces which are used for steam generation and/or electric power production. The most common type of coal-burning furnace in the electric utility industry is the dry, bottom pulverized coal boiler. When pulverized coal is burned in a dry, bottom boiler, about 80 percent of the unburned material or ash is entrained in the flue gas and is captured and recovered as fly ash. The remaining 20 percent of the ash is dry bottom ash, a dark gray, granular, porous and a predominantly sand-sized 12.7 mm ( $\frac{1}{2}$  in). The material is collected in a water-filled hopper at the bottom of the furnace [5]. These types of ash which are conveniently stored in the vicinity of the power plant are a great risk to the environment. Such a threat has triggered numerous research studies that aim at the beneficiation of these wastes. Although the fine fly ash can be used as an additive in the cement industry, utilization of the bottom ash that contains unburned carbon and coarse particles is quite limited.

Karasu et al. [6] found that borax waste could be used as a melting aid and could substitute for K-feldspar in the production of wall tile glazes. These authors also found that borax beneficiation waste could be added at amounts as high as 13.5% in the frit of floor tiles. Kartal et al. [7, 8], Ediz et al. [9, 10], Karasu et al. [11, 12], Boncukcuoglu et al. [13], Uslu et al. [14] and Koseoglu et al. [15] have discussed the possible use of boron beneficiation wastes as additives in ceramics

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and building materials. The general conclusion of these studies reveals the significant potential of these wastes as additives in ceramic production since they lower the melting point and increase the structural strength.

In this study, the influence of tincal and bottom ash additions on the physical properties and microstructure of ceramic materials was investigated. The findings show that with the addition of bottom ash in ceramic materials, environmental hazards can be prevented or decreased.

## Materials and methods

### Materials

The materials used in the experimental studies were tincal, bottom ash and a reference body. Tincal was obtained from Eti Mine Kirka Boron Works (Eskisehir, Turkey) and the bottom ash was obtained from Soma Power Plant (Manisa, Turkey). Standard granule wall tile body material, a product of a spray dryer, is used as a reference. The chemical compositions of materials are given in Table 1.

Tincal contains mainly  $B_2O_3$ ,  $SiO_2$ ,  $Na_2O$ ,  $MgO$  and  $CaO$  chemical compounds. Tincal melts completely at  $741^\circ C$  and forms a glassy phase [16]. Tincal mainly includes the minerals dolomite, illite, chlorite, kaolinite, tincal, ulexite, calcite and quartz. Bottom ash includes quartz, mullite, plagioclase, portlandite, illite, muscovite, kaolinite, calcite, melilite, hematite [17], and unburned coal [18]. The melting point of bottom ash varies between  $1200$ – $1400^\circ C$  depending on its alkaline oxide, earth alkaline oxide, silicates and aluminates concentrations [19, 20].

### Methods

Tincal was air dried for 72 h and bottom ash was dried at  $110^\circ C$  for 24 h in an electric furnace. These materials were milled in a ball mill to obtain a particle size of below  $63 \mu m$ . The body compositions were mixed for 20 minutes in a ball mill to obtain an ideal

mixture. The samples were then moisturized to 5 % for better compressing. Bodies of  $100 \times 50 \times 10$  mm dimensions were formed by uniaxial pressing at 40 MPa.

Firing under laboratory conditions is different than firing in an industrial furnace. In this study, the bodies were fired in industrial furnaces. Thus, any disadvantages resulting from the firing process was eliminated. The shaped samples were dried at  $110^\circ C$  for 24 h and then were fired in refractory roller industrial furnace for 34 minutes at  $1195^\circ C$ . Ten different formulations were prepared by mixing different amounts of reference body, bottom ash and tincal (Table 2).

The batches were named from TO and BA. In the TO batches, the amount of bottom ash was constant at 10 % whereas the amount of tincal varied from 1% to 5 %. The remaining part was the reference body. The samples of BA contained 3% tincal, with bottom ash varying from 5 to 25%, and reference body. The samples were subjected to shrinkage, water absorption, and modulus of rupture tests.

## Determination of physical parameters of tiles

### Linear shrinkage

The linear shrinkage of the samples was determined after drying and firing. The total shrinkage, which is the linear shrinkage from the wet state to the fired (sintered) state, was also determined. The linear shrinkage is calculated as follows:

$$LS = \frac{L_w - L_f}{L_w} \cdot 100 \quad (1)$$

where  $LS$  is the linear shrinkage percent,  $L_w$  wet length of the body (mm),  $L_f$  is the fired length of the body (mm).

### Water absorption

The sintered tiles were dried to constant weight, cooled to room temperature, and then weighed. The tiles were immersed in distilled water and boiled for three hours. After the heating was halted, the tiles remained immersed in the water for 24 h. The tiles were then taken out and the excess water was removed from their surfaces by wiping with a damp cloth. The tiles were again weighed. The water absorption was calculated using the formula:

$$WA = \frac{wf - wi}{wi} \cdot 100 \quad (2)$$

where  $WA$  is the water absorption (%),  $wi$  is the dry mass (g),  $wf$  is the fired mass (g).

**Table 1.** Chemical composition of reference, tincal, and bottom ash

Oxides	Reference, wt %	Tincal, wt %	Bottom ash, wt %
$SiO_2$	68.00	5.73	37.30
$Al_2O_3$	17.86	1.11 ( $R_2O_3$ )	15.19
$Fe_2O_3$	1.87	-	3.41
$TiO_2$	1.54	-	0.40
$CaO$	1.30	6.21	24.93
$MgO$	6.30	5.96	1.92
$Na_2O$	1.82	11.32	1.04
$K_2O$	0.60	-	1.14

**Table 2.** Body compositions of reference, TO and BA batches (wt. %)

Formulation	R	TO <sub>1</sub>	TO <sub>2</sub>	TO <sub>3</sub>	TO <sub>4</sub>	TO <sub>5</sub>	BA <sub>1</sub>	BA <sub>2</sub>	BA <sub>3</sub>	BA <sub>4</sub>	BA <sub>5</sub>
Reference	100	89	88	87	86	85	92	87	82	77	72
Tincal	-	1	2	3	4	5	3	3	3	3	3
Bottom ash	-	10	10	10	10	10	5	10	15	20	25

### Fired strength

The fired (sintered) tiles were measured to determine the sample width and the sample thickness. The measured tiles were put onto a strength machine. The distance between the supports was measured and then samples were crushed using the strength machine. The breaking load of the tile was read from the machine. The fired strength was calculated using the following formula:

$$FS = \frac{3FL}{2bh^2} \quad (3)$$

$FS$  is the fired strength (MPa),  $F$  is the breaking load (N),  $L$  is the distance between supports (mm),  $b$  is the sample width (mm), and  $h$  is the sample thickness (mm).

## Results and discussion

### Water absorption and fired strength

The results showed that water absorption of tiles decreased with an increase in tincal amount. (Fig.1). Tincal is a strong flux and completely melts at a low temperature. The molten tincal particles in the tile body coalesced with others and fill the pores in the body. Hence, the addition of tincal decreases water absorption. Similar results have been reported in the literature [21, 22]. Further addition revealed no significant variation in the water absorption values. Results show that the fired strength of tiles increased with increasing tincal addition. However, no significant change is observed in the fired strength of tiles with more than 2% tincal.

The water absorption and fired strength of BA batches are shown in Fig. 2. It is observed that the water absorption decreases sharply up to 5% bottom ash. On the contrary, further addition of bottom ash causes water absorption to increase sharply.

The addition of bottom ash to the body revealed very little change in the fired strength of the bodies. Although the fired strength of the bodies decreased with the addition of bottom ash up to 5%, the fired strength increased with further addition of bottom ash. The reason for this may be mixing bottom ash with tincal. The addition of bottom ash to the body may lead to a decrease in the

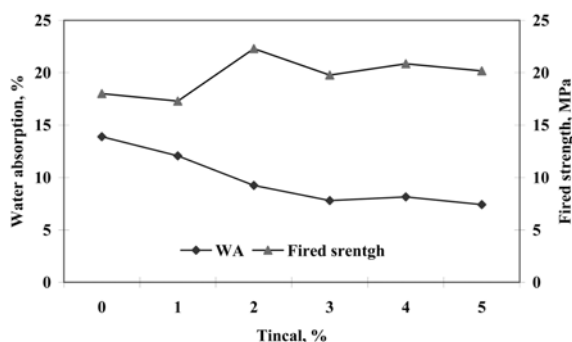


Fig. 1. Water absorption and fired strength of TO batches. (contains 10 % bottom ash)

fired strength. This reduction may be prevented by the flux action of tincal. Earl and Sinton [23] reported that compared to porcelain compositions, less glassy phase forms in the bottom ash bodies, thereby inhibiting sintering (filling of pores).

### Linear shrinkage

The linear shrinkage of TO batches is shown in Fig. 3. Results show that the fired strength decreases sharply with the addition of up to 1% tincal. However, no significant change is observed in the linear shrinkage of tiles with increasing tincal.

The linear shrinkage of the BA batches is shown in Fig. 4. The linear shrinkage of the bodies decreased sharply with up to 10% bottom ash addition. Any further addition of bottom ash has no effect on the linear shrinkage.

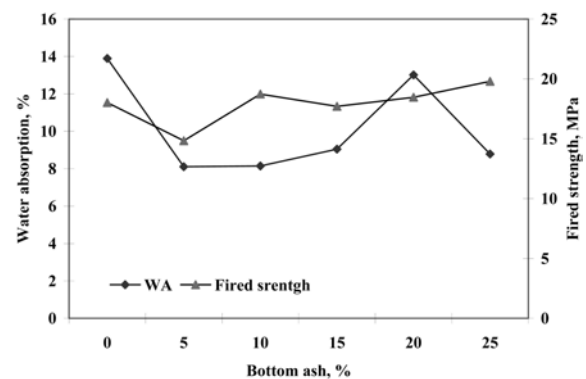


Fig. 2. Water absorption and fired strength of BA batches. (contains 3 % tincal)

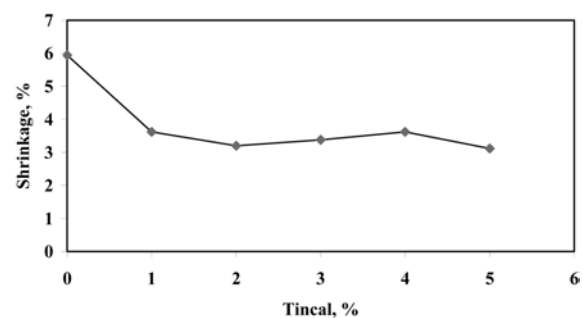


Fig. 3. Linear shrinkage of TO batches. (contains 10% bottom ash)

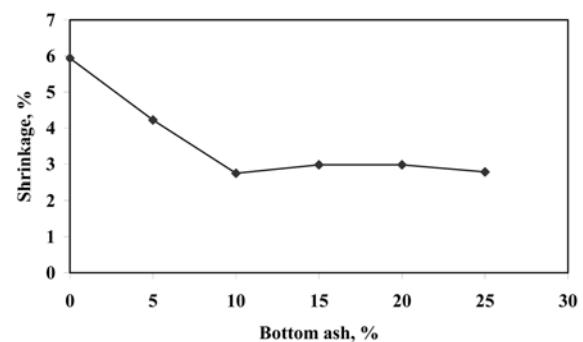
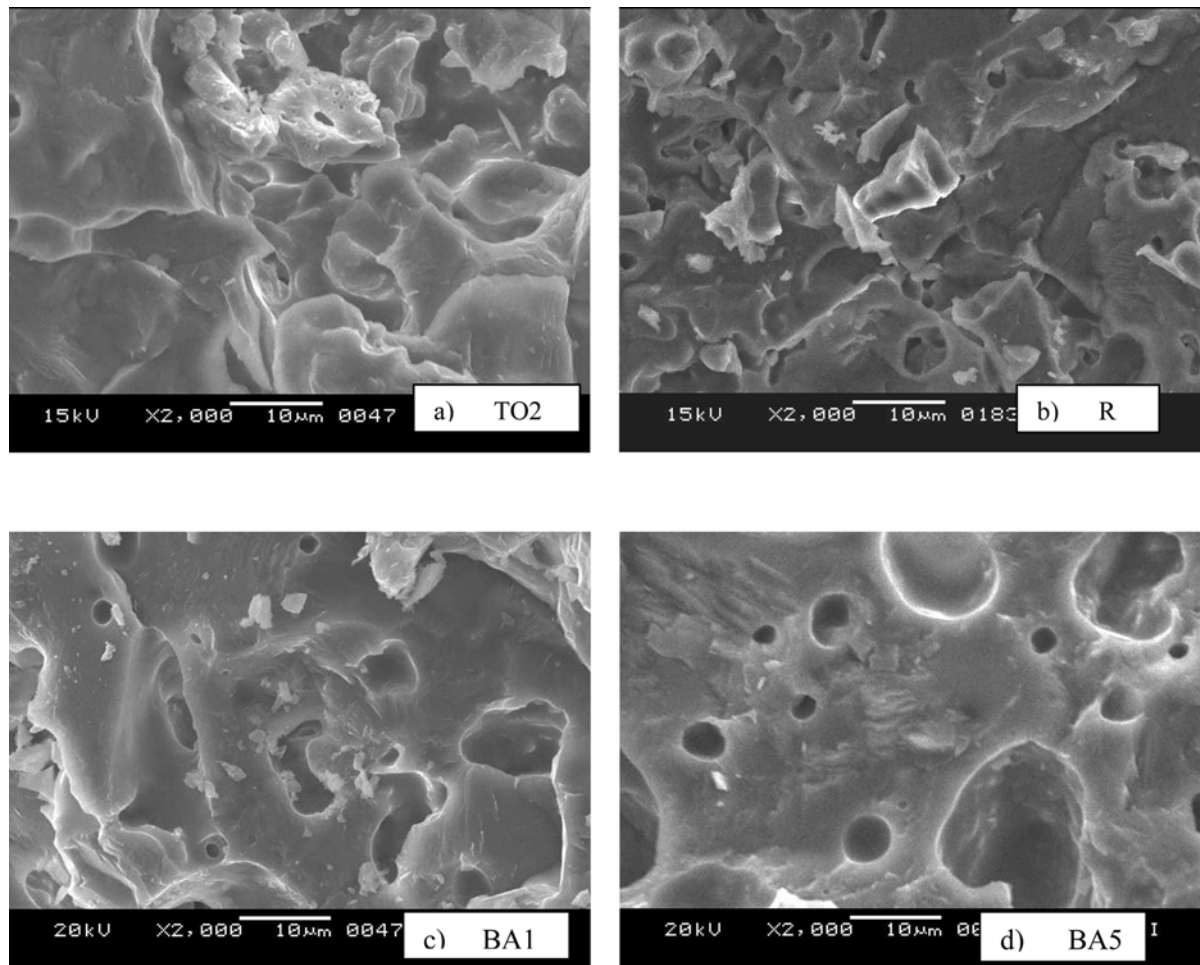


Fig. 4. Linear shrinkage of BA batches. (contains 3% tincal)



**Fig. 5.** SEM micrographs of bodies a) TO2, b) R, c) BA1, d) BA5.

The bottom ash leads to a decrease in linear shrinkage of the ceramic body, which may be due to the non-plastic material properties of the bottom ash. Plastic materials are clays in the body, which directly affect the amount of shrinkage of the body. Drying shrinkage increased with the amount of clay present. When shaping water is added to the clay body, it becomes very malleable due to the plasticity of the clay. Shaping water causes expansion in the clay body. However, the clay body shrinks after drying.

### Microstructural analysis

The microstructure of tiles (TO2) containing tincal is very uniform. The tiles have a fairly smooth surface a homogenous distribution of porosity, a high density, and are well sintered. The particles are closely connected, which makes their interfaces invisible. It was observed that the reference (R) surface is more porous, granular and rougher than those tiles containing tincal (TO2) (Fig. 5a and Fig. 5b). The microstructure of BA5 is much smoother, denser, well sintered and less porous than that of BA1 (Fig. 5c and Fig. 5d).

### Conclusions

The experimental studies showed that water absorption and linear shrinkage of the body decreased with increasing tincal content. However, the fired strength increased with increasing tincal content. Crack formation was not observed in the tiles containing tincal. Tincal caused an increase in the glassy phase of the body, which leads to a decrease in the open porosity of ceramic body. Due to its low melting point, tincal can be used as a flux material in the production of tiles. Thus the tiles can be fired at lower temperatures. Tincal has a positive effect on the physical properties of the ceramic body.

Water absorption of the bodies decreased with the addition of bottom ash, which caused improvement in the physical properties of tile body. However, due to increasing water absorption of the bodies, a large amount of bottom ash leads to unfavorable effects. Since linear shrinkage decreased with increasing bottom ash content, linear shrinkage of the bodies had a positive effect. Due to the fact that bottom ash didn't contain plastic material, fired shrinkage of the bodies decreased. Because the incorporation of bottom ash

improved the physical properties of the ceramic, coal bottom ash can be used in ceramic tile body production. Hence, the cost of ceramic tiles would decrease and the environmental hazards of bottom ash would be prevented. The incorporation of up to 3% of tincal, together with bottom ash of up to 15% in the wall tile body composition has a favorable effect on the physical properties of the bodies.

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### References

1. Eti Mine Works General Management ([www.etimaden.gov.tr](http://www.etimaden.gov.tr))
2. Batar, T., Kahraman, B., Cirit, E., Celik, M. S., *International Journal of Mineral processing*, 54 (1998) 99 -110.
3. Mark Burleson, *The ceramic glaze handbook*, Lark Books, 2003.
4. Robert. Noyes, 1993, *Pollution Prevention Technology Handbook*, Published by William Andrew Inc.
5. Recep Boncukcuoglu, M. Tolga Yilmaz, M. Muhtar Kocakerim, Vahdettin Tosunoglu, *Cement and Concrete Research* 32 (2002) 35-39.
6. Karasu B., G. Kaya ve R. Kozulu, (in Turkish), *Proceeding of the 1<sup>st</sup> International Boron Symposium*, Kutahya, Turkey, 2002.
7. Kartal, A., Evcin, A., Kavas, T., (in Turkish), *I. Boron Symposium*, 2005, Ankara, Turkey.
8. Kartal, A., Alaca, M., Emrullahoglu, O. F., *Key Engineering Materials*, 264-268(2004) 1649.
9. Ediz, N., Issi A. and Yurdakul, H., *Key Engineering Materials*, 264-268(2004) 2465.
10. N. Ediz, H. Yurdakul and A. Ýssi, *Key Engineering Materials*, 264-268(2004) 2457.
11. Karasu, B., Kaya G and Karalar, M., *Key engineering Materials*, 264-268(2004) 2457.
12. Karasu, B., Kaya, G, Kozulu, R., *Key Engineering Materials*, 264-268 (2004) 2505.
13. Boncukcuoglu, R., Kocakerim, M.M., Kocadagistan, E., Yilmaz, M.T., *Resources, Conservation and Recycling*, 37 (2003) 147-157.
14. Uslu, T., Arol, A.I., *Waste Management*, 24 (2004) 217.
15. Koseoglu, K., Bayca, S. U., *Proceeding of the 1<sup>st</sup> International Boron Symposium*, Kutahya, Turkey, 2002.
16. Stefanov, S., Batschwarow, S., *Ceramic Glazes*, Bauverlag Gmbh, Weiesbaden und Berlin, 1988.
17. Vasiliev, S.V., Vassileva, C. G, Karayigit, A.I., Bulut, Y., Alastuey A., and Querol, X., *International Journal of Coal Geology*, 61 (2005) 35-63.
18. Benavidez, E., Grasselli, C., Quaranta, N., *Ceramics International*, 29 (2003) 61.
19. Appendino, P., Ferraris, M., Matekovitis, I., Salvo, M., *Journal of the European Ceramic Society*, 24 (2004) 803.
20. Olgun, A., Erdogan, Y., Ayhan, Y., Zeybek, B., *Ceramics International*, 31 (2005) 153.
21. Menezes, R. R., Ferreira, H.S., Neves, G A., Lira H. L. and Ferreira H. C., *Journal of the European Ceramic Society*, 25 (2005) 1149-1158
22. Kniess, C T, Milanez, K W, Kuhnen, N C, Riella, H G Segadaes, A M Qualicer 2004. *VIII World Congress on Ceramic Tile Quality*. Vol.III; 2004
23. D. A. Earl and C. W. Sinton, *The Center for Environmental and Energy Research (CEER) at Alfred University*, May 2003 CEER Annual Meeting.