# Eczacıbaşı Yapı Grubu Bozüyük Kampüsünden Çıkan Atıkların Geri Dönüşümü

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### Özet

Anahtar kelimeler Atık, CO<sub>2</sub> salınımı; Karo üretimi. Bu çalışmada, porselen karo pişmiş atığı ile birlikte SSG ve kaplama malzemeleri üretiminden çıkan arıtma filterpres atığının porselen karo bünye reçetesinde kullanılabilirliği araştırılacaktır. Standart bir bünye karışımından başlayarak, atıkların kullanıldığı farklı reçeteler çalışılmış ve bunlardan iyi sonuç veren iki tanesi bu çalışmada anlatılmıştır. Atıkların hazırlanan kompozisyonun sinterleme, pişme küçülmesi, renk değişimi özellikleri üzerindeki etkisi çalışılmıştır ve analiz sonuçlarına göre reçeteye ilave edilebilecek optimum miktarlar belirlenmiştir. Söz konusu proje gerçekleştikten sonra, daha az doğal kaynak kullanımı dolayısı ile reçete maliyetleri azalmıştır, Bozuyuk kampusunde bulunan atıkların kullanımı sonucu kampüse taşınan hammadde miktarı azalmıştır ve bunun sonucu olarak taşımacılık sebebi ile ortaya çıkan emisyon azalmıştır.

# Recycling Ceramic Production Wastes of Eczacibasi Building Group Bozuyuk Campus

#### Abstract

*Key words* Waste; CO<sub>2</sub> emission; Tile production. The possibility of use of porcelain stoneware tile fired waste and purification filter press wastes which occur in the production of sanitaryware and coating materials, by their incorporation in a porcelain stoneware body mix, was studied. Starting from a standard body mix, several modified body mixes were prepared with these wastes and two of them was given in present study. The effects of wastes on sintering, firing shrinkage, water absorption, colour variation properties of prepared compositions was studied and the amount of optimum entry to recipes was identified by changing according to analysis results. When the subject project occurred, recipe costs decreased with lower natural resource use, raw material that was carried to campus decreased with utilization of wastes in Bozüyük campus, as a result,  $CO_2$  emission that was because of transporting decreased environmental and visual pollution and this helps to leave a cleaner environment the next generations.

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#### 1. Introduction

Sanitaryware articles areporcelain products generally produced from "vitreous china" and desired to have water absorption values of less than 0.5%. After firing, the major phases of vitreous china are mullite and glass; there is also a moderate proportion of unreacted silica, normally in the form of  $\alpha$ -quartz and minor amounts of porosity (Carty and Senapati 1998; Bernardin and Riella 2006; Tuncel et al. 2011). Sanitaryware ceramics constitute 7% of the world's ceramic market when monitored from the economic point of view.

Ceramic coating materials are basically divided into three classes; wall tiles, floor tiles and porcelain tiles. Wall tiles are ceramic tiles that are produced at a temperature of 1120 – 1150 °C, have high porosity and water absorption between 10-20 %. Floor tiles are fired at higher temperatures such as 1180 – 1190 °C for 30-45 minutes. Water absorption values of floor tiles are less than 3 %. Porcelain stoneware tiles have excellent properties due to their low water absorption and high mechanical strength (Biffi 1999; Sanchez et al. 2001; Tarhan 2010).

Coating materials and sanitarywares consist of clay, quartz and feldspar. These raw materials are taken directly and undergo size degradation process. At the end of this, they are shaped by being mixed in a specific composition. Then, they undergo firing process in order for them to obtain a specific durability and hardness. They will undergo various decoration and glazing processes if needed. 22 million square meter floor, wall and porcelain tiles and 4.200.000 sanitarywares are produced in Eczacıbaşı Bozüyük campus in a year. As it can also be seen in production amounts, there is a huge raw materials income to the campus every year and at the end of the production, high amount of various wastes occur. Under the current circumstances, 10.000 ton/year floor tile, 9.000 ton/year wall tiles and 24.000 ton/year porcelain tile raw, 18.000 ton/year fired, 18.000 ton/year (12.000 ton tile, 6.000 ton sanitaryware) purification filter press waste and 12.000 ton/month waste water occur in coating material production. Raw waste, fired waste, filter press waste and wastewater occur in sanitaryware production. Raw wastes that occur in sanitarywares and tile production by recycling in recipes in their own body. Fired wastes of floor tiles and wall tiles are mixed and used in recipes at specific proportions with the help of previous studies. Sanitaryware fired wastes are reused in cement factories. However, porcelain tile fired wastes and sanitaryware and tile filter press wastes and wastewater that occur during production have not been recycled so far. These wastes unfortunately are sent to Local Garbage Collection Centers. Use of porcelain tile fired waste, and purification filter press wastes, which occur in the production of sanitaryware, in recipes was researched in this study. The effects of wastes on sintering, firing shrinkage, water absorption, colour variation properties of prepared compositions was studied and the amount of optimum entry to recipes was identified by changing according to analysis results.

## 2. Materials and Methods

In this study, porcelain stoneware body composition was prepared by using industrial raw materials and wastes. Chemical analyses of the porcelain tile green wastes, fired wastes and purification filter press wastes are shown in Table1.

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	Purification	Porcelain	Dorcolain tilo
Compositions	filter press	tile fired	groon wastes
	wastes	wastes	green wastes
Al <sub>2</sub> O <sub>3</sub>	17.56	20.16	18.94
SiO <sub>2</sub>	61.79	66.54	64.76
Na <sub>2</sub> O	2.59	2.79	2.63
K <sub>2</sub> O	1.16	1.77	1.48
MgO	0.41	1.36	1.02
CaO	4.55	3.48	2.72
ZnO	0.95	0.14	-
TiO <sub>2</sub>	0.37	0.6	0.53
$Fe_2O_3$	0.78	1.46	0.79
ZrO <sub>2</sub>	2.36	0.52	-
BaO	0.22	-	-
$P_2O_5$	-	0.05	0.1
L.O.I <sup>a</sup>	7.26	1.13	7.03

<sup>a</sup>; L.O.I. is loss on ignition.

A formulation, used for the industrial production of porcelain stoneware tiles, was chosen as a standard body mix. Starting from the standard body composition, different amounts of porcelain tile fired waste and purification filter press wastes which occur in the production of sanitaryware and coating materials, were added into the system.

50 wt. % of new body formulation were prepared by using raw materials used in standard recipe. Other part of 50 wt. % of body formulations were prepared by using wastes in different ratio. The ratios of wastes in recipes are shown in Table 2. The new compositions were denoted as W1 and W2.

 Table 2.Ratio of (wt %) used body mix and wastes in the recipes

Compositions	W1	W2
Standart body mix	50	50
Porcelain tile green wastes	40	30
Porcelain tile fired wastes	5	10
Purification filter press wastes	5	10

Creating a new oxide by adding the amount of waste composition, especially alkali and alkaline earth total amount supplied is a value close to the standard recipe. Chemical analyses of the standard body and new compositions are shown in Table3.

Table 3. Chemica	I compositions	(wt%) o	f the recipes
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Compositions	STD (Mean) (S.D.)	<b>W1</b> (Mean) (S.D.)	<b>W2</b> (Mean) (S.D.)
Al <sub>2</sub> O <sub>3</sub>	17.0±1.0	17.97±0,05	18.10±0,05
SiO <sub>2</sub>	67±2.0	65.82±1.0	65.76±1.0
Na <sub>2</sub> O	3.2±0.2	2.92±0.1	2.93±0.1
K <sub>2</sub> O	0.80±0.2	1.14±0.1	1.14±0.1
MgO	0.69±2	0.85±1	0.84±1
CaO	2±1.0	2.99±0.5	2.63±0.5
ZnO	-	0.12	0.11
TiO <sub>2</sub>	0.53±0.01	0.53±0.005	0.52±0.005
Fe <sub>2</sub> O <sub>3</sub>	0.58±0.01	0.72±0.005	0.76±0.005
ZrO <sub>2</sub>	-	0.15	0.3
BaO	-	0.01	0.02
P <sub>2</sub> O <sub>5</sub>	0.1±0.01	0.04±0.005	0.09±0.005
L.O.I		3.2	2.95

New compositions were prepared by wet grinding. Slips were dried at 110°C. The powders obtained were moisturized with 5%wt water. The pellets with 50 mm diameter and 6 mm thickness were prepared by uniaxial pressing at a forming pressure of 44 bar (Nannetti Press, Hydraulic Laboratory Press Mignon S, Italy). Finally, samples were single fast fired in a roller industrial furnace under industrial conditions (Heat treatment was 44 min and the peak temperature was 1210°C).

% Water absorption 
$$(w_a) = \frac{w_w - w_d}{w_d} \times 100$$
 (1)

Sintering temperatures of the compositions were determined by flex point (i.e., temperature at which densification rate is maximum) analyses as stated by Paganelli (2002) using the optical dilatometer (Misura 3.32, ODHT-HSM, Expert System Solutions, Italy). Open porosity were determined by water saturation under vacuum (ISO 10545-3) by using related equation (Eq. (1)).

Furthermore, the colour of fired body samples was measured using a UV-Vis spectrophotometer (Minolta 3600d, Japan) and the chromatic coordinates as L\*, a\*, b\*. Samples were polished by using polishing machine (Metkon-Forcipol-300-1N). After polishing the sample microstructures were examined by scanning electron microscopy (SUPRA-Zeiss-50). In addition, as a function of the compositional changes firing shrinkage, water absorption and chromatic co-ordinates variations of porcelain stoneware tile were compared and discussed.

## 3. Results and Discussion

Table 4 presents some of the important properties of the investigated bodies fired under industrial conditions. A comparison of the standard porcelain stoneware body with the W1 and W2 was made according to the main technological properties measured. The L\*-value (lightness) of the standard body is higher than that of the new bodies. This is expected since there appears to be higher amount of impurity in the new bodies thus giving more darkness to the system.

When the fired residual amount is increased (W2), linear shrinkage decreases. Because the fired product completed most of the reactions during the previous firing, material amount, which causes loss and therefore contract by creating reaction in the new composition, decreases.

**Table 4.** Technological properties and chromatic co-ordinates of the tile bodies

Formulation	Firing Shrinkage (%)	Water absorption (wt%)	L*	a*	b*
Standart body	6.8	0.05	59.37	3.21	9.63
W1	6.8	0.038	58.40	2.95	9.43
W2	7	0.026	57.62	1.58	7.90

When the raw material starts reaction, gas comes out and bubble forms in the body. These bubbles move to the surface as they are heated. With the use of fired residuals, possibility of bubble formation, which will move to the surface and cause open porosity on the surface, decreases. The decrease of water absorption value with the increase of the fired residual amount in the recipe can be explained this way.

Increasing of fired waste affected the microstructural properties of porcelain tile (Fig. 1).

The images in Figure 1 verify that the amount of the pore, which comes to the surface, decrease with the use of fired residual. W2 recipe, where the most fired residual is used, has the least open porosity scatter.

## 4. Conclusions

In this study, it has been shown that porcelain stoneware tile fired waste, and purification filter press wastes which occur in the production of sanitaryware and coating materials, can be successfully used in porcelain tile body formulation. It has been found that if amount of oxides is not changed too much by adding wastes instead of raw materials, properties of resulting tile (water absorption, lightness...) also doesn't change. In addition, it has been found that using fired waste decreases the formation of porosity and also the water absorption. When the subject project occurred, recipe costs decreased (432.000 TL/yil) with lower natural resource use, raw material that was carried to campus decreased with utilization of wastes in Bozüyük campus (68.000 TL/yıl), as a result, CO2 emission (25.000 kg) that was because of transporting decreased. Decreasing the waste amount that needs to be sent to local garbage collection centers decreased environmental and visual pollution and this helps to leave a cleaner environment the next generations.





**Figure 1.** SEM micrographs of the polished porcelain stoneware tiles.

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