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The Recycling of Ceramic Sludge Waste to Produce Alternative Eco-Products in Ceramic Tile Factory

Kağan Kayacı[1], Hasan Ergin[2], Ali Altıntaş[1], Yıldız Yıldırım[1], Çiğdem Yiğit Pala[1], Mert Kılıç[1], Emrah Durgut[1]

Abstract

In ceramic production vast amount of green process waste are created. Green process waste in other words, sludge waste creates a big environmental problem. It can create water pollution as well as create environmental problems having a big physical change of the stored area, Therefore the uses of sludge waste in the process as raw material or producing environmentally friendly eco-products are vitally important.

Firstly, the long term samples were taken in order to observe the fluctuation of the collected waste in Kaleseramik Factory in Turkey. Then, the characterization of sludge wastes was carried out by using XRF and XRD. Different recipes prepared using green process waste, fired granite tile waste and the other components to make different products. The vitrification behaviour of products was evaluated using a double-beam optical non-contact dilatometer. XRD was also used for phase analysis of fired product. Microstructural and micro chemical characteristics of the fired bodies were also observed using scanning electron microscopy (SEM). Finally; the physical, mechanical and color properties of formulations; such as water absorption, linear shrinkage, breaking strength and chromatic coordinates were measured. The results showed that it is possible to develop porcelain tile body with suitable technological properties by using an appropriate mixture of process wastes in the body composition. The fully use of sludge waste and fired granite tile waste eliminates environmental problems and also provides the cost advantages of alternative products.

Keywords: sludge waste, fired granite tile waste, porcelain tile

1. INTRODUCTION

Ceramic industry has been developing rapidly in Turkey as it has gained an important position due to its increasing production capacity and export rate in World market in recent years. However, it is vitally important to take the market in long term under the conditions of increasing competition in World market. Therefore, the production of ceramic tiles with low cost has become a major goal while providing high quality products in accordance with customer satisfaction. It is necessary to search and develop alternative raw material resources instead of using high cost raw material resources which becomes more difficult to supply and more costly. Wastes generally emerge as a secondary product during the production process. In the ceramic production process, wastes are created especially in grinding, glazing and purification phases. Inevitably, the reuse of created wastes in the production gives advantages for both economic and environmental aspects. It minimizes the usage of high cost raw materials and reduces also the amount of waste that creates potentially environmental pollution. This also provides

[2]*Corresponding author: [2]Hasan Ergin:İstanbul Teknik Üniversitesi Maden Mühendisliği Bölümü, 34469, Maslak/İstanbul ,Türkiye* hergin@itu.edu.tr

[1]*Kağan Kayacı:Kaleseramik AR-GE Merkezi Çan/Çanakkale,Türkiye* kagankayaci@kale.com.tr

energy savings as well as the cost of managements of waste produced. In this frame; the characterisation and the possibility of use of waste water produced in ceramic production was sought by researchers [1]. The research have been done for using granite cutting residue wastes in industrial porcelain tile recipes instead of feldspar [2] . The usability of Borax waste as an additive in wall tile texture was also studied [3]. The use of granite sawing wastes in the production of ceramic brick and tile production [4] and the use of slag and borax by products in glaze production were studied [5] . The usage of wastes and by products in ceramic sector has been presented in Table 1.

The purpose of this study is to search the usage of wastes that are produced in the ceramic tile production process. This paper sets out the full results of the uses of sludge waste and fired granite waste as raw materials for producing environmentally friendly eco-products.

Table 1. Wastes and their usage areas in Ceramic Sector

Sanitary Ware Wastes	Ceramic Tile Texture – Ceramic Health Equipment
Fired Ceramic Tile Wastes	Ceramic Tile Texture
Glass Wastes	Porcelain Stoneware Tile Production-Glass Ceramic Production-Wall and Floor Tile Textures
Boron Wastes	Frit Production-Boron silicate Glass Production-Brick Production-Building Brick and White Brick, Wall, Floor Textures and Glazes
Natural Stone and Marble Wastes	Wall and Floor Tile Textures-Porcelain Stoneware Tile Production

2. MATERIALS AND EXPERIMENTAL STUDIES

2.1 Material Characterization

In the ceramic production processes, green process waste and other types of wastes are created. As a results of a long term measurement, it was found that around 100 ton/day green process waste created in the refinement facility of in Kaleseramik Inc. that is one of the biggest ceramic tile producers in the World. Additionally, 30 ton/day of the granite tile waste is cretaed which could not be added to traditional ceramic bodies because of color differences. It is proposed to utilise these wastes with possible highest rate in order to produce some alternative products called as Eco-Products.

Firstly, in order to characterize the sludge waste in other words, green process waste, a sampling scheme was planned and applied. Five different samples with the intervals of five days were collected in order to observe the fluctuations and to determine the chemical compositions of samples and also long term mixed samples. The chemical analysis of each samples taken at different time period and mixed sample, that was carried out by XRF method, is illustrated Table 2.

As seen in Table 2, there are not important fluctuation in the chemical composition of the samples taken at different time. All samples are the similar chemical compositions.

Furthermore, in order to observe the technological properties of sludge waste, the physical, mechanical and color properties such as water absorption, linear shrinkage, breaking strength and chromatic coordinates were measured for the three samples which are taken in the first three weeks of sampling works. The results are shown in Table 3.

The XRD analysis of samples have shown that all samples iclude the same minerals that are quartz, mullite, albite and zircon. The shrinkage of samples were changed between 6,71 and 9,07.

In the search of formulation of eco-product; the fired granite waste is also proposed to be used with posssible highest amount. Therefore, the chemical analysis of fired granite waste is carried out as is shown in Table 4. The fired granite waste grindability is also determined for estimation of eco-product cost. The used granite waste in the recipe had the size of +45 µ sieve residue is 2,95 % . The total alcali content of fired granite waste is around 4,60%. The addition of fired granite waste attributes as an alcali source to the proposed recipes.

Table 2. Chemical compositions of the green process wastes (wt %)

Oxide (mass %)	Sample-1	Sample-2	Sample-3	Sample-4	Sample-5	Mixtured sample
L.o.I	5,60	5,88	4,54	6,88	5,53	5,45
SiO2	64,92	64,62	63,95	63,33	63,44	63,83
Al2O3	17,01	17,02	18,70	16,75	18,43	16,16
TiO2	0,26	0,27	0,27	0,31	0,25	0,32
Fe2O3	1,32	1,71	1,62	1,65	1,26	1,46
CaO	3,56	3,18	3,27	3,81	4,32	4,11
MgO	1,71	1,83	1,32	1,70	0,83	1,54
Na2O	2,48	2,30	2,65	2,17	2,38	2,43
K2O	1,85	2,06	2,20	2,06	1,91	2,00
Total	98,71	98,87	98,52	98,66	98,35	98,79
ZrO2	1,37	1,06	1,09	1,05	1,25	1,11
SO4	0,12	0,15	0,17	0,14	0,18	0,18
C	0,17	0,24	0,29	0,28	0,30	0,12

Table 3. Technologcal properties of ceramic sludge waste

Items	Waste Sludge-1	Waste Sludge-2	Waste Sludge-3
Temperature (°C)	1175	1175	1175
Time (min.)	40	40	40
Fring shrinkage (%)	6,71	9,07	8,55
Water absorption (%)	0,02	0,02	0,01
L	60,47	60,69	61,62
a	1,44	1,69	1,66
b	8,05	8,4	8,22
XRD	quartz	quartz	quartz
	mullite	albite	albite
	zircon	mullite	zircon
	albite	zircon	mullite

Table 4. Chemical compositions of the fired granite waste (wt%)

L.o.I	SiO2	Al2O3	TiO2	Fe2O3	CaO	MgO	Na2O	K2O	Total
0,56	68,62	22,43	0,35	0,68	1,31	1,07	3,56	1,04	99,65

The other two basic components are clay and kaolin as are in all ceramic tile products. However, their usage rate is intented to be kept as minimum for reaching the low cost product target. The chemical composition of used kaolin and clay is shown in Table 5.

Table 5. Chemical compositions of the kaolin and the clay (wt%)

Oxide (mass %)	L.o.I	SiO2	Al2O3	TiO2	Fe2O3	CaO	MgO	Na2O	K2O	Total
Clay	7,91	59,25	25,29	1,11	2,68	0,34	0,59	0,56	1,95	99,68
Kaoline	2,27	75,15	14,1	0,21	1,35	0,36	0,32	0,83	5,22	99,81

2.2 Developed Recipes and Tecnological Feautures

Among the many experimental trials carried out, the four selected formulations (A, B,C,D) allow us to produce eco-product which is shown in Table 6. A different amounts of clay, kaolin, green process waste and fired granite wastes are added to compose of different bodies as seen in Table 6. The composition of developed for reciepes and their physical properties such as (water absorption, firing shrinkage, colour properties) are shown in Table 6. The techonogical feautures of formulated bodies were determined in details. In order to determination of thermal behaviors of developed formulas; Differential Thermal Analysis Method (DTA) has been used. The vitrification behavior was evaluated by using a double-beam optical non-contact dilatometer. XRD was also used for phases analysis to fired bodies. Microstructural and micro chemical characteristics of the fired bodies were observed using scanning electron microscopy (SEM). Finally, the physical, mechanical and color properties of formulations such as the water absorption, linear shrinkage, breaking strength and chromatic coordinates were measured as they have been fired at 1175 °C for 44 minutes. The results have shown that the water absorption values were measured less than 0.5%, which comply with the porcelain tile standard, and shrinkage values were also close to each other.

Table 6. Different body recipies for producing eco-products

Items	A	B	C	D
Waste sludge (%)	50	60	50	65
Fired granite waste (%)	20	10	10	10
Kaolin (%)	10	10	20	10
Clay (%)	20	20	20	15
Temperature (°C)	1175	1175	1175	1175
Time (min.)	44	44	44	40
Fring shrinkage (%)	8,57	8,35	8,39	9,07
Water absorption (%)	0,04	0,09	0,06	0,05
L	59,14	59,19	58,41	58,95
a	2,55	2,61	2,64	2,69
b	11,67	11,62	11,93	11,70

However, all these four body compositions comply fully with the standarts, the formula of D was selected to be used to produce eco-product due to the use of maximum waste rate in further tests for industrial scale production.
In formula D; 75% waste, %10 kaolin and 15% clay are used. The chemical compositions of developed body D is analyzed by XRF method and the results is shown in Table 7.

Table 7. Chemical compositions of developed body (D) (wt%)

Oxide	L.o.I	SiO2	Al2O3	TiO2	Fe2O3	CaO	MgO	Na2O	K2O	SO4	ZrO2	Total
[Mass-%]	4,60	64,11	19,92	0,48	1,55	2,07	1,62	2,11	2,48	0,17	0,81	99,92

3- RESULTS AND DISCUSSION

The physical and technological properties of developed recipes were already given in Table 6. Industrial scaled production of developed recipe of D has been done in size of 45x45 cm and 30x60 cm tile, in the firing cycles of at 1175°C / 44 minutes as it was the firing condition for developing suitable recipies in the laboratory study.

The vitrification behavior was measured using a double-beam optical non-contact dilatometer.The vitrification features of developed bodies and the standart glazed porcalainbody are shown in Figure 1. It has been observed that the bod containing wastes shrinked more when it is compared to the standard glazed porcelain body.

Additionally, in order to identify the phases formed after firing, XRD analyses have been carried out that is shown in Figure 2. The analyses of XRD have shown that the developed body with wastes has the mullite, quartz and albite phases as these phases are also present in the standard body. However, an additional zircon phase has been observed in the developed body. The amount of feldspar crystal in the glassy phase of the developed body is less than standard body. However, it fullfills all the requriemets defined in the standards.

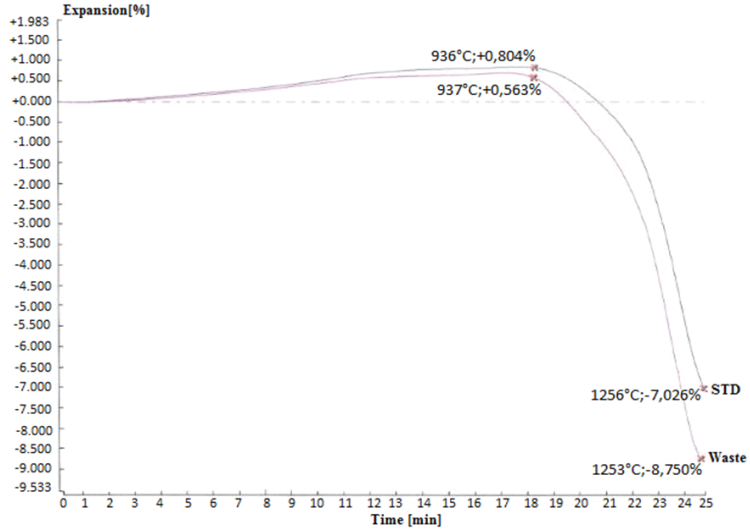


Figure 1. Dilatometric curves of the standard glazed porcelain tile and investigated formulations (cycle at1175 °C, 44 min.)

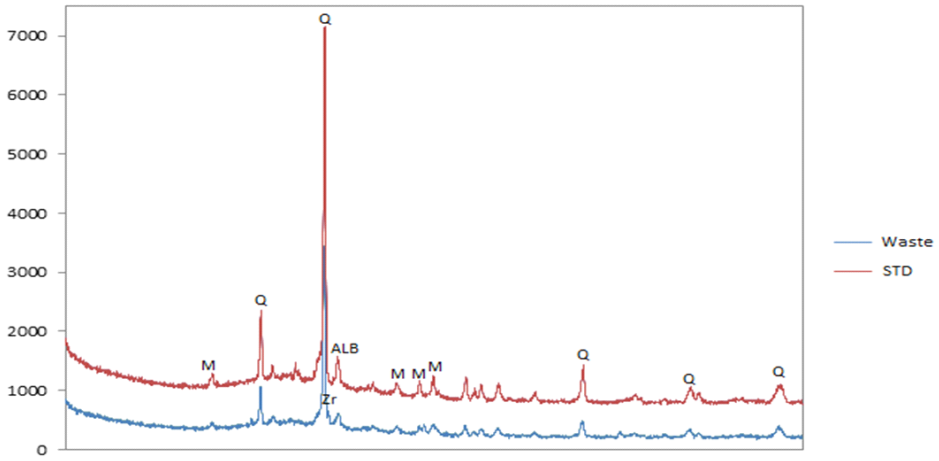
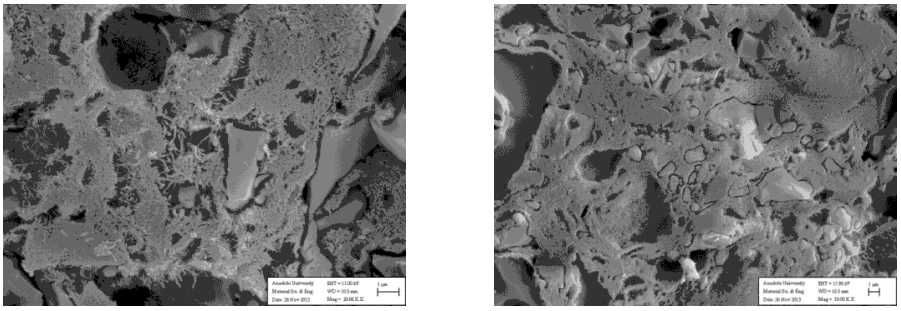


Figure 2. XRD spectra of the standard glazed porcelain tile and investigated formulations

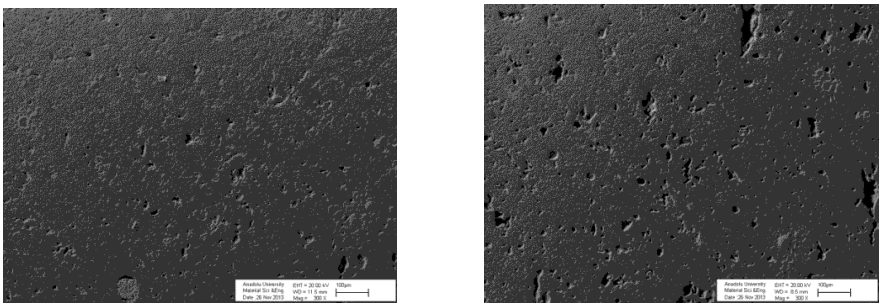
M: Mullite, Q: quartz, Zr: zircon, A: Albite

According to SEM analiysis of developed eco-product body and standart body; as seen in Figure 3.(a),(b) and Figure 4. (a), (b) respectivelly, both structure and their porosity are similar. The mullite cyristals are existed in both products.



(a) (b)

Fig 3. SEM micrographs on polished surfaces of the waste body (a) and standard body (b)



(a) (b)

Fig 4. SEM micrographs on polished surfaces of the waste body (a) and orj. body (b)

An example photo of the two different commercial eco-products canalso be seen in Figure 5.



Fig 5. Some examples for Eco-products

4. CONCLUSION

As a result of this study, it is convenient to produce eco-products comply with ISO 13006 standards. The total amount of the waste usage can be as high as 75%. It provides substansial cost advantages int the raw material costs as well as reducing the environmental pollution. In order to minimize the fluctations of the waste that could be homogenized hence the sludge waste and fired granite waste can be used for the long-term in the production of eco-products.

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