RECYCLING OF GREEN PROCESS WASTE IN PORCELAIN TILE

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1. INTRODUCTION

This paper describes a research project carried out on the possible reuse of mud (sludge) from the wastewater treatment plant of a local tile company in commercial ceramic tile formulations. The tile manufacturing process consists of a series of stages which can be summarized as follows: storage of raw materials, body preparation, shaping, drying of the green body, glaze preparation and glazing, firing, sorting and packaging. All process wastes come from all the production stages. As is well known, the use of waste materials has also become more important recently due to the reduced availability of high quality raw materials. From the literature, a considerable part of recent studies is related to the replacement of traditional raw materials in tile formulations with wastes such as glass, and others such as mud, boron waste, sludge waste, fly ash, etc. [1-6]. At Kaleseramik, annual production of mud from the process water purification plant is around 36.000 tons/year; at the moment this waste is disposed of in a suitable field within the company.

2. EXPERIMENTAL STUDIES

As a result of the studies done, it was discovered that 100 ton/day green process waste occurred in the refinement facility. Additionally, usage of fired granite waste, which could not be added to traditional ceramic bodies because of colour differences, was targeted. First, the chemical compositions of the wastes that occurred at different times were analyzed by the X-RF method in order to control their stabilities. For the determination of thermal behaviours, the Differential Thermal Analysis Method (DTA) was used. The fired granite waste to be used in the composition was milled for 3 hours in the cylindrical mill after it had been reduced to under 1 mm in the mill in the storage area; and -150μ+45μ 2,95 was obtained. Different body compositions were formed by crushing various amounts of clay, kaolin, green process waste and fired granite wastes with certain amounts of electrolyte addition. The prepared bodies were then fired under glazed production conditions 1175°C/45'. In order to determine the thermal properties of the developed bodies TGA/TG measurements were carried out. The vitrification behaviour was evaluated using a double-beam optical non-contact dilatometer. XRD was also used to determine the phases after firing. The microstructural and micro chemical characteristics of the fired bodies were observed using scanning electron microscopy (SEM). Finally, the physical, mechanical and colour properties of the formulations, such as water absorption, linear shrinkage, breaking strength and chromatic coordinates, were measured.

3. RESULTS

The chemical compositions of mixtures of fired granite waste and green process wastes obtained at different times for five days and separately were analyzed by the X-RF method. Table 1 and Table 2.

Oxide [Mass %]	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Mixtured Sample 1	Sample 6	Sample 7	Sample 8	Sample 9	Sample 10	Mixtured Sample 2
L.o.I.	5,60	5,88	4,54	6,88	5,53	5,46	5,46	5,43	5,20	5,43	5,33	5,59
SiO_2	64,92	64,62	63,95	63,33	63,44	63,83	63,63	64,00	64,80	63,61	64,77	64,18
Al_2O_3	17,01	17,02	18,70	16,75	18,43	16,16	18,45	18,10	17,11	17,55	20,00	16,80
TiO_2	0,26	0,27	0,27	0,31	0,25	0,32	0,26	0,28	0,22	0,23	0,17	0,38
Fe_2O_3	1,32	1,71	1,62	1,65	1,26	1,46	1,03	1,43	1,24	0,94	1,17	1,25
CaO	3,56	3,18	3,27	3,81	4,32	4,11	4,07	3,56	3,53	3,85	2,99	3,23
MgO	1,71	1,83	1,32	1,70	0,83	1,54	0,62	1,00	1,37	1,35	1,83	2,07
Na_2O	2,48	2,30	2,65	2,17	2,38	2,43	2,37	2,50	2,64	2,49	0,15	2,70
K_2O	1,85	2,06	2,20	2,06	1,91	2,00	1,90	1,85	2,04	1,70	1,75	1,85
Total	98,71	98,87	98,52	98,66	98,35	98,79	97,79	98,15	98,15	97,15	98,16	98,42
ZrO_2	1,37	1,06	1,09	1,05	1,25	1,11	2,13	1,55	1,45	2,75	1,45	1,49
SO_4	0,12	0,15	0,17	0,14	0,18	0,18	0,17	0,12	0,16	0,16	0,18	0,17
%C	0,17	0,24	0,29	0,28	0,30	0,12	0,23	0,21	0,16	0,32	0,37	0,22

Table 1. Chemical compositions of the green process wastes (wt%).

Oxide [Mass %]	L.o.I.	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	MgO	Na_2O	K_2O	Total
	0,59	68,62	22,43	0,35	0,68	1,31	1,07	3,56	1,04	99,65

Table 2. Chemical compositions of the fired granite waste (wt%).

Based on these results, it was determined that the stabilities of the wastes obtained at different times could be assured by making a mixture. Analysis of the XRD results showed the presence of quartz, mullite, albite and zircon peaks. In the next phase, by analyzing the behaviours of wastes from different dates when they are fired alone, their water absorption, colour, shrinkage and resistance values were controlled. As a result, it was determined that their water absorption values changed between 0,01-0,02; however their shrinkage values presented variability between 6,5% and 9,0%. Considering these values, body formulations were developed, in which wastes belonging to different times were used in various rates. Besides waste, clay and kaolin were used in the formulations. The chemical compositions of the developed bodies were analyzed by the X-RF method. Table 3. Physical characteristics such as water absorption, shrinkage and colour of the developed bodies were controlled by firing at 1175 °C for 45 minutes. The results showed that water absorption values were less than 0.5%, which is the standard value for porcelain tile, and shrinkage values were close to each other.

Oxide [Mass %]	**L.o.I.**	**SiO_2**	**Al_2O_3**	**TiO_2**	**Fe_2O_3**	**CaO**	**MgO**	**Na_2O**	**K_2O**	**SO4**	**ZrO2**	**Total**
	4,60	64,11	19,92	0,48	1,55	2,07	1,62	2,11	2,48	0,17	0,81	99,92

Table 3. Chemical compositions of developed bodies (wt%).

As a conclusion of the laboratory studies, an industrial-scale production trial was performed by firing the bodies, which were prepared by a convenient formulation, sized 45x45 cm and 30x60 cm, in firing cycles 1175°C/45 minutes. It was established that the tiles that were produced at the end of the trial complied with ISO 13006 Standards. Moreover, physical tests of samples and standard glazed porcelain tiles were done, and the vitrification behaviour was evaluated using a double-beam optical non-contact dilatometer. Figure 1. As a result of the analysis, it was observed that the body of wastes shrank more compared to the original glazed porcelain body. Additionally, in order to identify the phases formed after firing, XRD analyses have been done. Figure 2. On analysis, the results allowed mullite, quartz and albite phases to be identified in both bodies. However, an additional zircon phase was also seen in the body of wastes. Moreover, the amount of waste feldspar crystal in the glassy phase of the body of wastes was identified to be less.

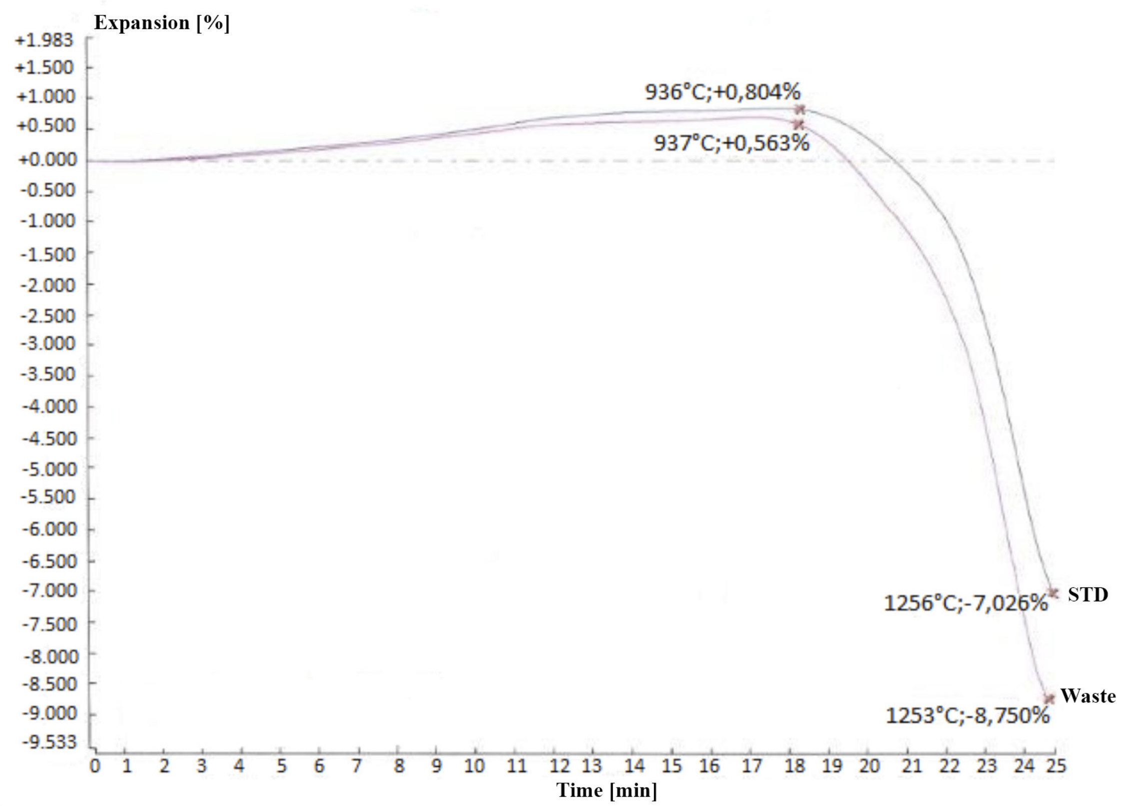

Figure 1. Dilatometric curves of the standard glazed porcelain tile and studied formulations (cycle: 1175 °C, 45 min.).

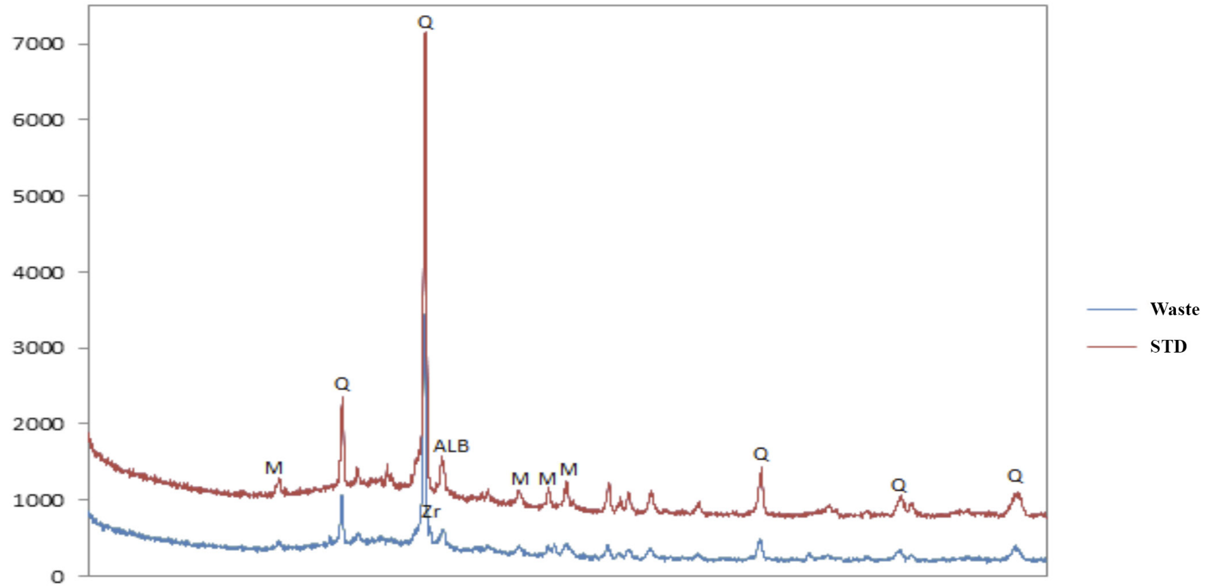

Figure 2. XRD spectra of the standard glazed porcelain tile and studied formulations. M: Mullite, Q: quartz, Zr: zircon, Alb: Albite.

4. CONCLUSION

As a result of this study, glazed porcelain tile production that complies with the standards was realized as had been the aim, by using maximum amounts of green process waste and fired granite wastes. The most important problem that might emerge in the product, which was obtained by using 75% waste in its body, was the variability of the arising sludge content with time. Because of this variability, it is possible for the end product to experience fluctuations in its shrinkage and colour values. It is expected that the variability in question will decrease to a minimum level by accumulating the wastes and doing a large scale homogenization process.

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