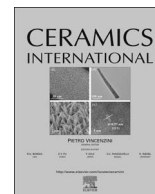




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Reusing sanitaryware waste products in glazed porcelain tile production

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ABSTRACT

Reusing the waste products generated in ceramic manufacturing is an environmentally responsible and sustainable approach. This study aims to protect natural resources, minimise raw material costs and manage waste-generated pollution by reusing the vitrified sanitaryware waste (VSW) products from Canakkale Kalebodur Seramik San. A. S. Six sample formulations were prepared under industrial conditions and compared with a standard tile body. The results indicated that using VSW in place of feldspar results in an increased firing shrinkage and decreased bending strength, whereas using VSW in place of pegmatite results in an increased bending strength and reduced thermal expansion coefficients. The reduction in the thermal expansion coefficients is an important finding that aids in meeting the dimensional and deformation requirements of porcelain tiles and also results in a slight lightening of the tile colour. This study shows that the fired VSW products can be used in glazed porcelain tile production as a sustainable and technologically, economically and environmentally suitable approach.

1. Introduction

Ceramic tiles are made of raw materials such as clay, kaolin, quartz and feldspar, and a continuous increase in their production has resulted in an increase in the requirement for large amounts of raw materials used in the manufacturing process. Therefore, an environmentally responsible and sustainable approach is to reuse the fired waste products generated in ceramic manufacturing as it helps to protect natural resources, minimise raw material costs and manage waste-generated pollution [1,2]. The Turkish Statistical Institute shows that 846.833 thousand tonnes of waste was disposed of without regulation in 2010 [2]. Such unregulated waste disposal results in serious problems related to the storage and transportation of the waste and also causes environmental pollution [3].

There are several studies in literature dealing with reuse of industrial waste and alternative raw materials in porcelain tile production. Most of these studies are under laboratory conditions. Torres et al. [4] show the effect of quartzite and granite sludges on ceramic floor tile compositions. The results of this study demonstrate that flexural strength values increased and water absorption decreased. Gennaro et al. showed some improvements in technological properties in their study [5], but the high slip viscosity, the worse powder compressibility, and more darkness in colour related with higher iron oxide of zeolite-feldspar epiclastic rocks are unsuitable for industrial production. Rajamannan et al. showed that fly ash develops the densification, with

higher compressive strength, lower porosity and water absorption [6]. Although the most critical issue in using fly ash in the ceramic industry is its stability of chemical composition, there is no mention of this in this study.

Vitrified sanitaryware waste (VSW) products are glazed products containing glassy phases, residual quartz and mullite [7]. The mullite present in sanitaryware wastes is suitable for use in ceramic bodies because of its high strength and low thermal expansion coefficient [7,8]. This study aims to investigate the use of sanitaryware waste products in vitrified porcelain tiles under industrial conditions.

2. Experimental procedure

All vitrified porcelain tile samples were prepared under industrial conditions and contained clay, kaolin, pegmatite, feldspar and VSW products. VSW was used in place of pegmatite in SG1, SG2 and SG3 bodies at concentrations of 5 wt%, 10 wt% and 15 wt%, respectively, and in place of Na feldspar in SG4, SG5 and SG6 bodies at concentrations of 5%, 10% and 15% by weight, respectively. VSW products were ground in an alumina mill for 18 h. The chemical compositions of the raw materials were determined using an X-ray fluorescence analyser (Panalytical Axios XRF, Kale Ceramic Research Centre). An industrial ceramic vitrified porcelain tile production formulation was selected as the standard (STD) composition. The raw materials were ground in a jet mill for 30 min. The tile masses obtained were pressed using a

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uniaxial press in a 50 mm×100 mm die at 320 kg/cm² pressure and then dried at 110 °C. The firing process was performed in an industrial rollerkiln at 1185 °C for 45 min (including cooling). Body lightness (L) and a*, b* colour values were determined using a colour measurement instrument (Minolta Konica, Kale Ceramic Research Centre). The sintering behaviour was investigated using an optical dilatometer (MISURA ODHT HSM 1600/80, Anadolu University). Heat treatment was performed in two stages. The green samples were first fired at 500 °C with a heating rate of 80 °C/min and then sintered at 1210 °C with a heating rate of 50 °C/min. X-ray diffraction (XRD) was performed to analyse the phases in the fired formulations using an X'Pert Pro MPD diffractometer (with CuK α radiation) at 40 kV and 30 mA. Samples were scanned from 2 θ =3–70° at a scanning rate of 2 °/min. The microstructures of the ceramic bodies were determined using scanning electron microscopy (SEM, Zeiss EVO 50EP, Anadolu University, Turkey). For the SEM–EDX analysis, polished sample surfaces were etched for 2 min in a 5% HF acid solution and then all samples are ultrasonically washed. After washing, the samples were dried and coated with Au and Pd. Bulk density was measured with mercury displacement method.

3. Results and discussion

3.1. Chemical analyses

The chemical analysis results of the raw materials are as shown in Table 1. While clay contributes to plasticity on the green body for shaping operation, kaolin promotes mullite formation. Sodium feldspar acts as a fluxing agent during the firing process, resulting in a liquid phase. It promotes mullitisation–developing densification. Quartz is a filler raw material. It also contributes to a reduction in shrinkage and deformation of fired bodies [9].

3.2. Technological properties

Technological properties of the samples are given in Table 2. The bending strength increased with an increase in the amount of VSW in SG1, SG2 and SG3 bodies; the firing shrinkage, in contrast, remained nearly constant. As shown in Table 2, a strong correlation exists between the bending strength and water absorption capacity of the SG1, SG2 and SG3 bodies. However, there was a considerable increase in the water absorption capacity and firing shrinkage values for SG4, SG5 and SG6 bodies and a decrease in their bending strengths; therefore, substituting VSW in place of feldspar is suitable only at a ratio of less than 5 wt%. Mullite content in VSW waste contributes to increase in strength of SG2 due to the dispersion–strengthening process. The relation among bending strength, chemical composition and microstructure was explained in detail in the SEM analysis section.

The colours of all the fired ceramic tile bodies were indicated as 'L', 'a' and 'b' values. L represented the brightest and darkest values, where L=100 indicated the brightest white and L=0 indicated the darkest black. The parameters a=0 and b=0 indicated true neutral grey values. Green and red colours were represented by (–a) and (+a) values,

respectively, and blue and yellow colours were represented by (–b) and (+b) values, respectively. L values were observed to increase with increasing VSW addition. This is an important finding in the development of low-zirconia glazes and engobe recipes. The results for the technological properties of the samples showed that VSW is more suitable for substituting pegmatite than feldspar in the chemical composition of ceramic tiles.

3.3. XRD analyses

XRD analyses of the sample bodies and VSW are shown in Figs. 1 and 2. The crystalline phases for both STD and SG bodies included a glassy phase, quartz, mullite, albite and a small amount of cristobalite crystals. Quartz in the fired tile bodies was a residual phase and mullite was formed during firing [10], whereas the cristobalite crystals in the investigated bodies originated from VSW.

The phase transformations in terms of chemical composition in all bodies during sintering were described. The removal of the physically adsorbed water took place until 100 °C. α - β quartz inversion of silica took place at 573 °C. Kaolinite loses the OH group, resulting in metakaolinite (Al₂O₃.2SiO₂) between 450 °C and 600 °C. At 1000 °C, peaks of mullite begin to appear and the silicate lattice totally collapses and a spinel structure is formed. Primary mullite crystals were formed. Above 1100 °C, albite are almost invisible due to the dissolution of albite to form a glassy phase [2]. The results are in full compliance with the chemical composition data and XRD analysis [2].

3.4. Sintering properties

The sintering behaviour of each body is shown in Figs. 3 and 4. Heat treatment was performed in two stages. First, the bodies were heated at 500 °C at a heating rate of 80 °C/min and then sintered at 1210 °C at a heating rate of 50 °C/min with a 10 min soaking time. The results showed that SG1, SG2 and SG3 bodies exhibited a similar sintering behaviour as that of the STD body, whereas SG4, SG5 and SG6 bodies exhibited a higher firing shrinkage than that of the STD body, as shown in Table 2. The sintering mechanism of porcelain tile bodies is viscous flow sintering. Glassy phase is formed during the firing process. Formation of glassy phase results in a decrease in specific surface area and porosity. While the surface tension of the liquid phase is responsible for the driving force, the sintering rate is controlled by the viscosity of liquid phase. Because the changes in the chemical properties of alumina silicate systems do not affect the surface tension, the sintering rate is mainly controlled by liquid phase viscosity [11,12]. The addition of alkali and alkaline earth oxides in SiO₂ glass cause a decrease in the glassy phase viscosity owing to more non-bridging oxygen sites [12]. While alkaline earth oxides with high atomic weight lead to a decrease in viscosity more than that of low atomic weight, this tendency is exactly the opposite for alkali oxides. At low temperature, alkaline earth oxides contribute to make a bridge over two non-bridging oxygen sites, therefore they increase the viscosity due to strengthen the network. The mixed alkali effect introduces two types of alkali ion into a glassy network. When one type of alkali ion in an

Table 1
Chemical analysis of the raw materials.

	LOI ^a	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	Na ₂ O	K ₂ O	ZrO ₂
Pegmatite	0.49	78.5	12.57	0.19	0.37	0.51	0.07	2.42	4.96	
Kaolin	6.36	65.41	19.27	4.48	1.12	0.14	0.29	0.27	2.31	
Clay A	7.97	60.75	24.62	1.91	1.31	0.34	0.56	0.42	1.99	
Na Feldspar	0.25	70.73	17.13	0.08	0.45	0.71	0.11	9.26	0.4	
Clay B	7.28	62.21	21.87	3.27	1.23	0.33	0.84	0.43	2.33	
Clay C	46.03	8.78	1.83	0.41	0.24	1.26	40.89	0.22	0.13	
VSW waste	0.88	68.58	21.96	0.78	0.80	0.75	0.40	3.13	1.22	0.29

^a LOI: loss on ignition

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