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## The Replacement of Seashells with Calcite in White Ceramic Glaze Preparation

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### Abstract

In this study, the effect of seashell utilization as a replacement for calcite on the surface features and optical properties of white ceramic glazes was investigated. As received seashells collected from Black Sea beaches of Samsun, Turkey and purified seashells at 700°C for 1 h were used as calcite replacement by 15 wt.%. Seashell powders were incorporated to white glaze compositions which are applied on the surface of different fired clay bodies such as red clay, chamotte, white and porcelain by dipping technique. Next, the glazed green bodies were sintered at 1100°C for 8 h. Following to TG-DTA, heating microscope, XRD and optical analysis, the obtained results exhibited that as received seashell powder (SP-1) was composed of calcite (CaCO<sub>3</sub>), whereas purified seashell powder (SP-2) comprised aragonite (CaCO<sub>3</sub>) and calcium oxide (CaO). The iron (hematite) content in red clay and the impurities in seashells composition caused specks and crawlings on the surface of glazed red clay bodies and of some glazes containing seashell, respectively. In generally, the higher CaO content in SP-2 enhanced gloss (60°) values, and whiteness values of most glazed surfaces were closed to each other. The color of chamotte bodies increased redness-greenness values. The variations in optical parameters were mainly associated with the difference in body compositions. SP-1 contained glaze, applied on porcelain body, was selected as optimal because that had 33 gloss value, high whiteness (87) and no surface defect. Therefore, the utilization of as received seashells by 15 wt.% as calcite replacement allows eco-friendly and cost-effective production of white ceramic glazes without any additional heat treatment.

**Keywords:** White Ceramic Glazes, Seashells, Calcite, Optical Properties, Clay Products

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## 1. INTRODUCTION

Glazes are stable glassy coatings applied to on ceramic surfaces in order to supply a protective layer to the ceramic body. Also, glazing provides the product with a range of technical properties such as waterproof, cleanability, chemically and mechanically resistance and aesthetic features like gloss, color and texture. These features generally vary depending on the chemical composition and firing parameters. The ceramic glazes can be classified according to production process, application area, composition and the optical properties of the finished surface. Optical properties (e.g., brightness, color and texture) of the product are the important criteria for the classification of finished surfaces [1,2].

Glazes consist of several oxides. Silicon dioxide is the glass former of a glaze composition, while alkaline and alkaline earth oxides act as fluxers, opacifiers or dyes. CaO is an inexpensive raw material, widely used in glaze compositions, that reduces the viscosity of glaze. Also, CaO provides hardness and durability to glazes [2-4]. In glaze compositions, CaO is obtained from calcium carbonate which has two polymorphs: calcite and aragonite. Although the crystal structures of calcite and aragonite are different from each other, both the strength and the density of aragonite is higher than calcite [5].

Seashells are natural materials that consist of calcium carbonate compressed between biopolymers. Calcium carbonate provides strength, hardness and toughness to the shell structures [6,7]. They are used as raw materials in ceramic glaze compositions due to the calcium carbonate content. Seashells collected from the beaches are composed of calcite phase.

The aim of the study was to investigate the surface features and optical properties of white ceramic glazes prepared with as received seashells and purified seashells as a replacement for calcite by 15 wt.%. The seashells were collected from Black Sea beaches of Samsun, Turkey. Next, the collected seashells were heat-treated at 700°C for 1 h to remove organics in their composition. Seashell powders were incorporated to white

glaze composition, and the prepared glaze compositions were applied on the surface of different fired clay bodies. Gloss values and coloring parameters of finished products were determined.

## 2. EXPERIMENTAL PROCEDURE

### 2.1. Body Preparation

For the preparation of fired bodies (25x25 mm), slurries were hand-pressed, dried and heat-treated at 800°C for 7 h under atmospheric conditions. Four different plastic slurry were used which contain red mud, chamotte mud, white mud and porcelain mud.

### 2.2. Preparation of Seashell Powders

The collected seashells from Black Sea beaches of Samsun, Turkey were firstly washed. Secondly, a part of as received seashell powders were subjected to heat-treatment at 700°C for 1 h in an electrically-heated furnace to remove organics in the composition. While the collected and washed (as received) seashell powders were called as SP-1, the heat treated (purified) seashell powders were called as SP-2. Finally, both SP-1 and SP-2 were crushed and ball-milled for 90 s. Differential Thermal Analysis (DTA) and Thermogravimetry (TG) of SP-1 and SP-2 were carried out using Simultaneous Thermal Analyzer (STA, 409 PC/PG, Netzsch) between 25°C-1200°C. The critical temperatures of compacted SP-1 and SP-2 (2x2x3 mm) were determined using a heating microscope (Misura, TA Instruments) between 400°C-1550°C. The thermal analysis were conducted under oxygen atmosphere.

### 2.3. Preparation of Glazes

In order to obtain glazes, SP-1 and SP-2 were incorporated to glaze composition. Seashell powders were used as calcium carbonate source. The recipes of glazes are given in Table 1. After ball-milling of glaze compositions for 30 min in alumina media, they were applied on the surface of different fired bodies such as red clay body (B1), chamotte body (B2), white body (B3) and

porcelain body (B4) by dipping technique [10]. After glaze application, the sintering of glazed bodies was performed at 1100°C for 8 h under atmospheric conditions.

Table 1  
Recipes of the glazes (wt.%)

Raw material / glaze code	G1	G2	G3
<b>K-Feldspar</b>	37	37	37
<b>Calcite</b>	15	-	-
<b>Kaolin</b>	8	8	8
<b>Flint</b>	37	37	37
<b>Bentonite</b>	3	3	3
<b>SP-1</b>	-	15	-
<b>SP-2</b>	-	-	15

The qualitative phase analysis of non-glazed bodies was carried out using X-Ray Diffractometer (XRD, Miniflex 600, Rigaku). The optical parameters of the glazed bodies were determined using a chromometer (CM-2300d, Konica Minolta) between wavelength range of 360 nm - 740 nm. During the study, "G" referred to glazing code and "B" referred to fired body code.

### 3. RESULTS AND DISCUSSION

#### 3.1. Characterization of Seashell Powders

Chemical composition and the qualitative phase analysis results of SP-1 and SP-2 were reported in prior study [8]. In still, the chemical composition (wt.%) of SP-1 and SP-2 are given again in Table 2. Both SP-1 and SP-2 were comprised mainly CaO and some trace elements. While SP-1 comprised only calcite (CaCO<sub>3</sub>; ICDD 05-0586), SP-2 included aragonite (CaCO<sub>3</sub>; ICDD 41-1475) and calcium oxide (CaO; ICDD 28-0775) crystalline phases. The polymorphic transition of calcite into aragonite occurred during purification (at 700°C for 1 h) [9]. The presence of CaO as a minor phase caused by the partial decomposition of calcium carbonate during the purification (organic removal) of SP-2 [10]. For this reason, loss on ignition (L.O.I) value below 1000°C of SP-2 was found 2 % less.

Table 2  
Chemical composition (wt.%) of SP-1 and SP-2

Comp.	SP-1	SP-2
<b>CaO</b>	54.32	56.22
<b>Na<sub>2</sub>O</b>	0.59	0.32
<b>SiO<sub>2</sub></b>	0.23	0.17
<b>Fe<sub>2</sub>O<sub>3</sub></b>	0.03	0.05
<b>SO<sub>3</sub></b>	0.06	0.05
<b>P<sub>2</sub>O<sub>5</sub></b>	0.01	0.01
<b>Al<sub>2</sub>O<sub>3</sub></b>	0.23	-
<b>BaO</b>	-	0.30
<b>SrO</b>	-	0.19
<b>L.O.I.</b>	44.52	42.69

TG-DTA curves of SP-1 are given in Figure 1. According to DTA and TG/DTG curves of SP-1, endothermic peak at 854.0°C were related with thermal decomposition of calcite [10]. A high mass loss (44.2 wt. %) occurred between room temperature and 900°C was related with the removal of moisture and CO<sub>2</sub> gas. TG-DTA curves of SP-2 are given in Figure 2. The endothermic peak at 842.5°C were related with the decomposition of aragonite. A high mass loss (43.5 wt. %) occurred again until the finishing of decomposition (900°C). The endothermic peak and total mass loss of SP-2 (842.5°C, 43.5 wt. %) was found lower than these of SP-1 (854.0°C, 44.2 wt. %) because of the reduced content of calcium carbonate during purification and the absence of the organics. Heating microscope curve of SP-1 is given in Figure 3. The sintering, softening and melting points were determined as 1052°C, 1394°C and 1440°C, respectively. Heating microscope curve of SP-2 is given in Figure 4. The sintering, softening and melting points were specified as 1358°C, 1414°C and 1440°C, respectively. The higher sintering temperature of SP-2 could be related with the presence of CaO which has significantly higher melting point (2572°C) than calcium carbonates (calcite:1339°C and aragonite:825°C) [11,12].

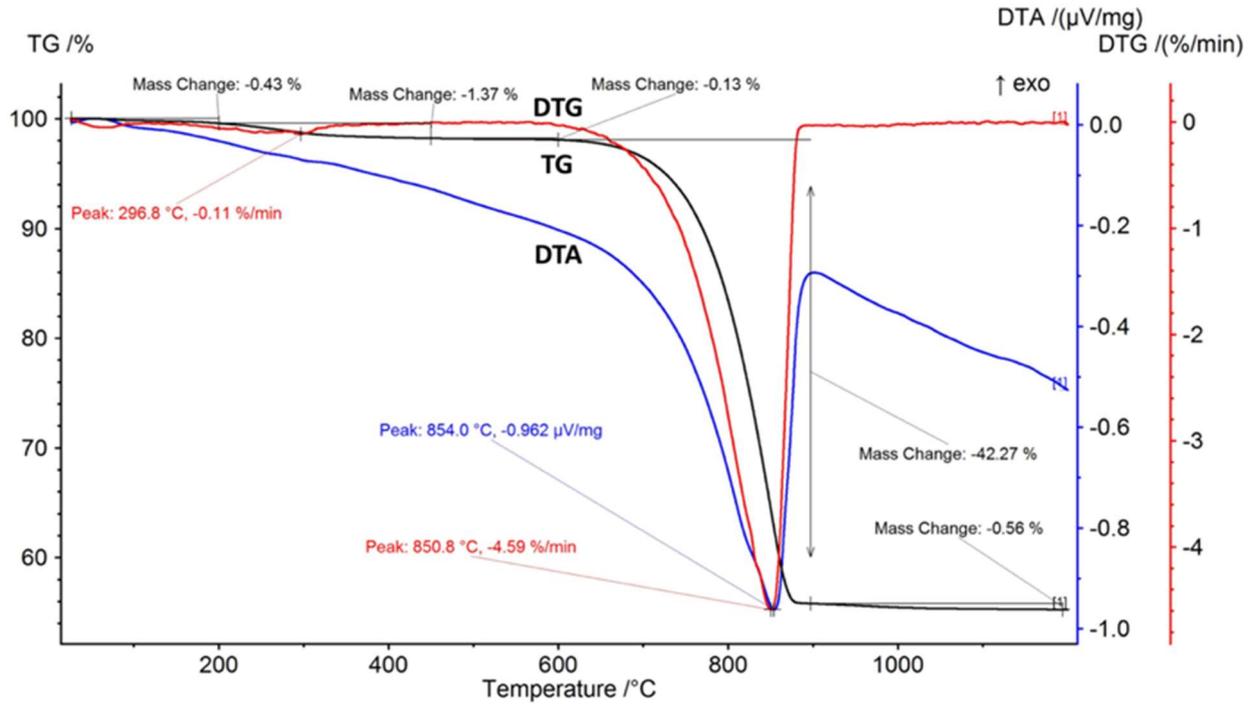


Figure 1 TG-DTA curves of SP-1

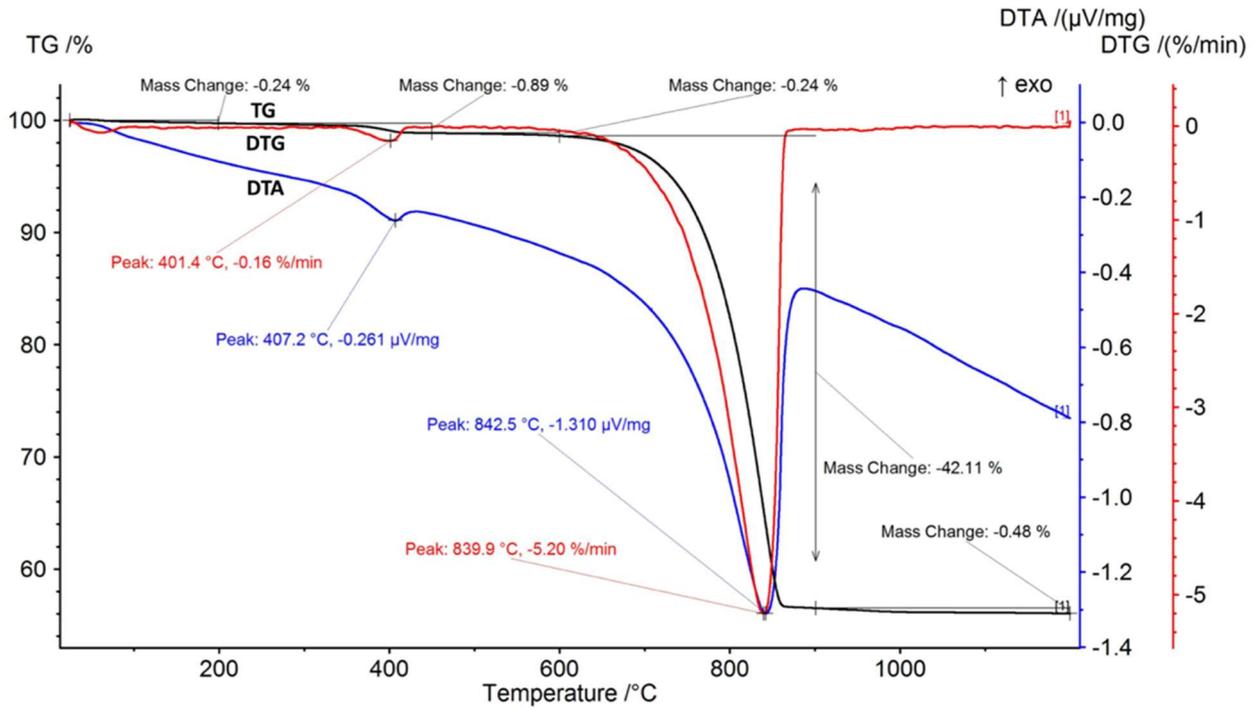


Figure 2 TG-DTA curves of SP-2

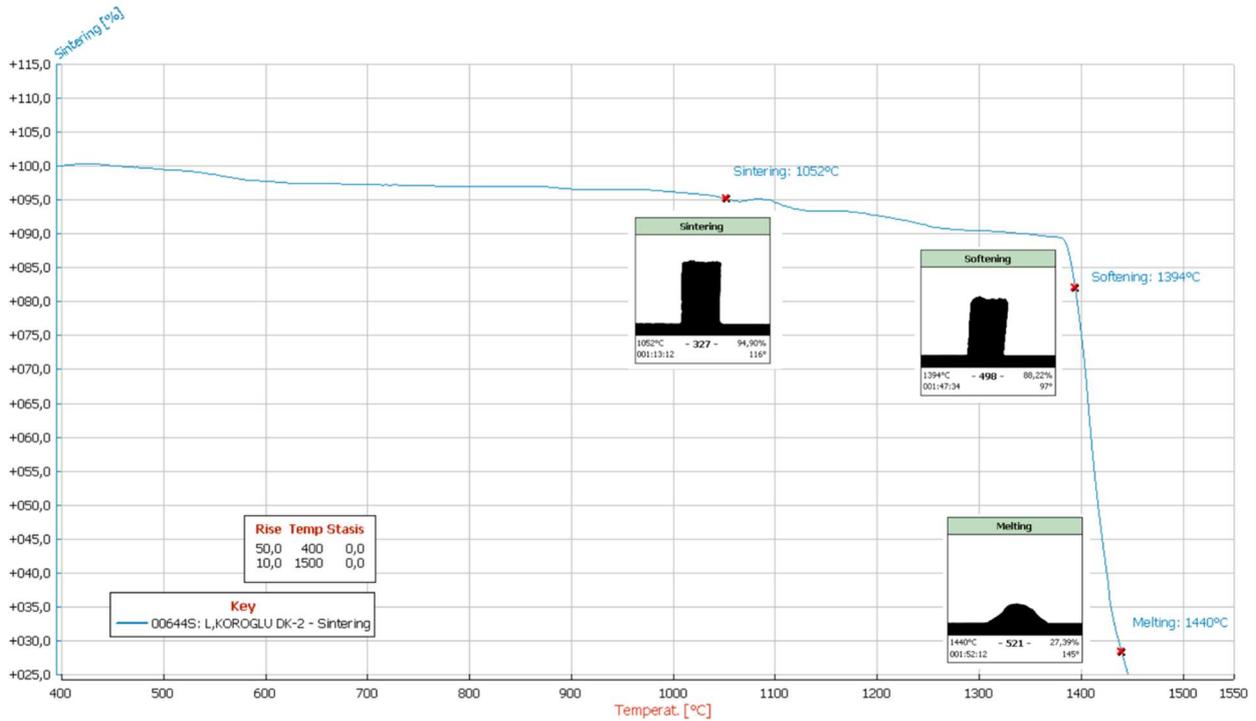


Figure 3 Heating microscope curve of SP-1

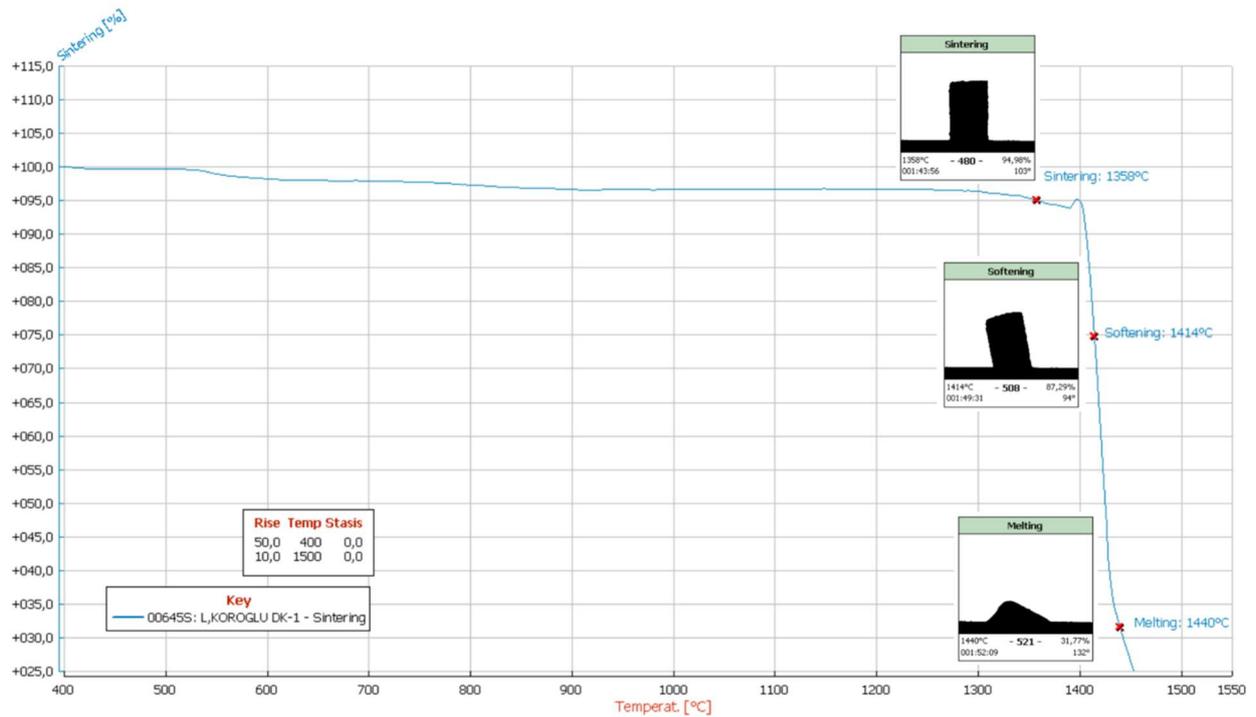


Figure 4 Heating microscope curve of SP-2

### 3.2. Characterization of Sintered Bodies

XRD patterns of sintered bodies are given in Figure 5. The phase analysis of bulk samples caused a shift in the patterns. Red clay body (B1) included quartz ( $\text{SiO}_2$ ), hematite ( $\text{Fe}_2\text{O}_3$ ) and albite ( $\text{NaCa}(\text{Si},\text{Al})_4\text{O}_8$ ) crystalline phases.

Chamotte body (B2) contained of quartz and mullite ( $\text{Al}_6\text{Si}_2\text{O}_{13}$ ). Both white body (B3) and porcelain body (B4) comprised quartz, albite and mullite. In contrast to other sintered bodies, red clay body contained  $\text{Fe}_2\text{O}_3$  as a minor phase besides the quartz and albite.

According to XRD patterns, all sintered bodies mainly contained quartz whereas aluminum silicate phases such as mullite and albite were

presented as minor crystalline phases. It caused by the higher peak intensity of quartz due to its higher structural factor [13].

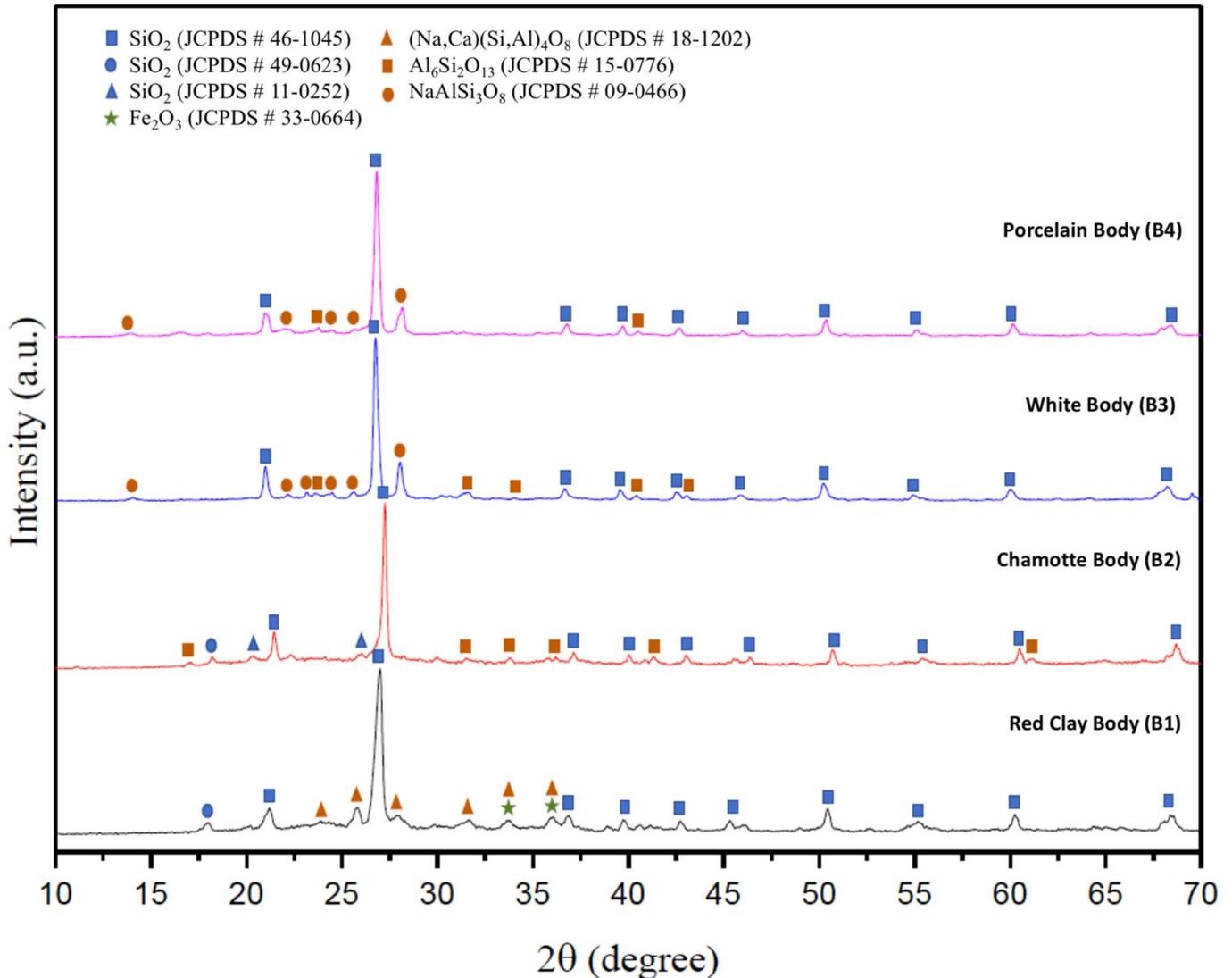


Figure 5 XRD patterns of sintered bodies

### 3.3. Characterization of Glazes

Digital images of sintered bodies are given in Figure 6. All glazes applied on B1 and B2 bodies provided non-homogenous opacity whereas, the dispersal of the glaze on B3 and B4 bodies were homogenous. The white color of these bodies could have inevitably affected the appearance. Some specks were observed on the surface of all B1 bodies. It was associated with the presence of iron (hematite) in B1 composition because it can pass into the glaze and cause a surface defect like that [3]. Also, the surface of G2-B2, G2-B3, G3-B3 and G3-B4 included crawling which is

unglazed or partially glazed area with irregularly shape, and breaks the uniformity of the fired glaze. The main factors causing crawling are glaze surface tension, the bond strength between the green glaze and the substrate, the shrinkage of the green glaze during drying, the lack of wetting of the body by the glaze and the presence of soluble salts which can lift the glaze away from the body in single-fire operations [3]. The crawling is seen only on seashell added glazes (G2 and G3). Even though the composition of all glazes was same (they contain same amount of calcium carbonate), the impurities were existed in G2 and G3 compositions (Table 2). Hence, the

reason of crawling could be the presence of impurities in seashells which alter surface tension and the bond strength between the glaze and body. Nevertheless, the surface of G2-B4 has not any defects.

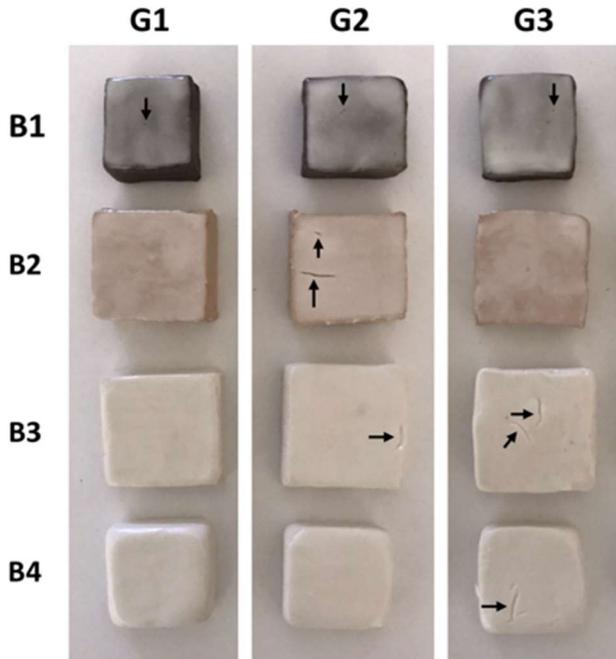


Figure 6 Digital images of sintered bodies

The color and gloss values of sintered bodies are given in Table 3, where  $L^*$  indicates whiteness,  $a^*$  redness-greenness and  $b^*$  yellowness-blueness. In generally, G3 glazed bodies had the highest gloss ( $60^\circ$ ) values. The maximum gloss value (45) was found for G3 glazed B2 body. It is known that a high gloss value is obtained from a smooth surface where the high percentage of the light is reflected off the surface at the same angle to the surface as the incident beam (specular reflection). On the contrary, some of the light is reflected at angles other than the incident angle (diffuse reflection) on a matte (opaque) surface. Hence, lower gloss values are obtained due to higher refractive index of the glaze resulting of surface roughness, crystals or phase separation [14]. Also,  $\text{CaCO}_3$  and  $\text{CaO}$  have white and grayish white color, diminish viscosity and retard crystallization during sintering [3,15,16]. Considering that, the higher gloss values of G3 glazed bodies were associated with the relatively higher  $\text{CaO}$  content in G3 composition.  $\text{CaO}$  as a fluxing agent could decrease the crystallinity degree of glaze and consequently, the diffuse

reflection was reduced. Moreover, the existence of  $\text{Na}_2\text{O}$  in G2 and G3 compositions as a fluxing agent could contributed to the increasing of glassy phase content in the glaze.  $L^*$  values of all glazed surfaces except G1-B1 were found closed to each other because G1 and G2 compositions included same calcite content even though G3 composition had  $\sim 2\%$  higher  $\text{CaO}$  content compared to G1 and G2, where the even small content of  $\text{CaO}$  has a dominant effect on the viscosity compared to whitening.  $a^*$  values of glazed B2 bodies were found remarkably higher. It showed the effect of red color of these bodies on coloring parameters. In this case, the thickness of the glazes could be lower due to the porous microstructure of chamotte bodies (B2) at sintering temperature ( $1100^\circ\text{C}$ ) [17] which have different composition (absence of albite phase) compare to other bodies. In addition, some variations in gloss,  $L^*$ ,  $a^*$  and  $b^*$  values were observed. It was thought that the reactions between the phases of green glazes and different bodies took place inevitably during sintering (at  $1100^\circ\text{C}$  for 8 h), and the composition, crystallinity degree and distribution of formed phases affected all optical parameters.

Table 3

Color and gloss values of sintered bodies

Sample Code	Gloss ( $60^\circ$ )	$L^*$	$a^*$	$b^*$
G1-B1	35.8	86.68	1.50	8.13
G1-B2	30.9	73.82	7.25	11.44
G1-B3	24.1	86.84	1.46	8.25
G1-B4	18.4	88.45	0.65	6.92
G2-B1	21.5	64.11	1.02	0.36
G2-B2	23.9	78.53	4.88	7.65
G2-B3	27.2	83.84	1.55	8.57
G2-B4	33.5	87.02	0.77	7.21
G3-B1	29.0	68.45	0.66	0.47
G3-B2	45.2	75.12	5.49	6.88
G3-B3	30.6	85.9	1.65	8.87
G3-B4	29.9	88.48	0.85	6.53

#### 4. CONCLUSION

In the present study, the effect of seashell utilization as a replacement for calcite on the surface features and optical properties of white ceramic glazes was investigated. As received seashells collected from Black Sea beaches of Samsun, Turkey and purified seashells at  $700^\circ\text{C}$

for 1 h was used as calcite replacement in powder form by 15 wt. % during white glaze preparation. Seashell powders were incorporated to white glaze compositions which are applied on the surface of different fired bodies such as red clay, chamotte, white and porcelain by dipping technique. Then, the glazed green bodies were sintered at 1100°C for 8 h under atmospheric conditions. The obtained results showed that as received seashell powder (SP-1) comprised calcite ( $\text{CaCO}_3$ ), whereas purified seashell powder (SP-2) included aragonite ( $\text{CaCO}_3$ ) and calcium oxide (CaO). The specks were observed on the surface of glazed red clay bodies, and the crawlings were detected on the surface of some glazes containing seashell. These were associated with the presence of iron (hematite) in red clay composition and the existence of impurities in seashell's composition. In generally, the gloss ( $60^\circ$ ) values were higher for SP-2 incorporated glazes, and whiteness ( $L^*$ ) values of most glazed surfaces were closed to each other. The main reason for gloss enhancement was higher CaO content as a fluxing agent. The color of chamotte bodies increased redness-greenness ( $a^*$ ) values. The variations in optical parameters were mainly associated with the difference in body compositions. SP-1 added glaze, applied on porcelain body, was selected as optimal because it had 33 gloss value, high whiteness (87) and no surface defect. The utilization of as received seashells by 15 wt.% as calcite replacement made white ceramic glaze production eco-friendly and cost-effective without any additional heat treatment.

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Conception:CP-LK, Supervision:CP, Materials:CP, Data Collection and/or Processing:CP-LK, Analysis:LK, Literature Review:CP-LK, Writer:CP-LK

### ***The Declaration of Ethics Committee Approval***

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## **REFERENCES**

- [1] D.W. Richerson, *The magic of ceramics*, John Wiley & Sons, New Jersey, 2012.
- [2] R. Casasola, J.M. Rincónand, M. Romero, "Glass-ceramic glazes for ceramic tiles: a review", *J. Mater. Sci.*, vol. 47, pp. 553-582, 2012.
- [3] R.A. Eppler and D.R. Eppler, *Glazes and glass coatings*, The American Ceramic Society, Ohio, 2000.
- [4] M. Burluson, *The Ceramic Glaze Handbook: Materials, Techniques, Formulas*, Lark Books, New York, 2003.

- [5] W.F. Tegethoff, *Calcium Carbonate: From the Cretaceous Period into the 21st Century*, Springer, Basel, 2001.
- [6] N.M. Neves and J.F. Mano, "Structure/mechanical behavior relationships in crossed-lamellar sea shells", *Materials Science and Engineering: C*, vol. 25, no. 2, pp. 113-118, 2005.
- [7] S. Chowdhury and P. Saha, "Sea shell powder as a new adsorbent to remove Basic Green 4 (Malachite Green) from aqueous solutions: Equilibrium, kinetic and thermodynamic studies", *Chemical Engineering Journal*, vol. 164, no. 1, pp. 168-177, 2010.
- [8] C. Peksen, L. Koroglu, and H. Kartal, "Utilization of Seashells in Matte Glaze Preparation", *International Journal of Applied Ceramic Technology*, pp. 1-8, 2020.
- [9] M. Ryu, H. Kim, M. Lim, K. You and J. Ahn, "Comparison of dissolution and surface reactions between calcite and aragonite in l-glutamic and l-aspartic acid solutions", *Molecules*, vol. 15, pp. 258-269, 2010.
- [10] K.S.P. Karunadasa, C.H. Manoratne, H.M.T.G.A. Pitawala and R.M.G. Rajapakse, "Thermal decomposition of calcium carbonate (calcite polymorph) as examined by in-situ high-temperature X-ray powder diffraction", *Journal of Physics and Chemistry of Solids*, vol. 134, pp. 21-28, 2019.
- [11] R.C. Ropp, *Encyclopedia of the Alkaline Earth Compounds*, Elsevier, Oxford, 2013.
- [12] R.J. Lewis, *Food Additives Handbook*, Springer, New York, 1990.
- [13] B.D. Cullity and S.R. Stock, *Elements of X-Ray Diffraction*, Addison-Wesley Publishing, Massachusetts, 1956.
- [14] R.A. Eppler and D.R. Eppler, "Controlling the Gloss of Leadless Glazes," *Ceram. Eng. Sci. Proc.*, vol. 16, no. 1, pp. 40-5, 1995.
- [15] A.R. Jamaludin, S.R. Kasim and Z.A. Ahmad, "The effect of CaCO<sub>3</sub> addition on the crystallization behavior of zno crystal glaze fired at different gloss firing and crystallization temperatures", *Science of Sintering*, vol. 42, pp. 345-355, 2010.
- [16] F. Cardelli, *Materials Handbook: A Concise Desktop Reference*, Springer-Verlag, London, 2008.
- [17] C.N. Djangang, A. Elimbi, U.C. Melo, G.L. Lecomte, C. Nkoumbou, J. Soro, J.P. Bonnet, P. Blanchart and D. Njopwouo, "Sintering of clay-chamotte ceramic composites for refractory bricks", *Ceramics International*, vol. 34, pp. 1207-1213, 2000.