

Evaluation of Pumice in Glaze Compositions for Ceramics

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Abstract

Pumice, identified as amorphous aluminium silicate, occurs as a result of volcanic activity and is a porous, spongy, volcanic, glassy rock that resists physical and chemical degradation. It is considered to be glass because it has no crystal structure. The use of pumice as a fluxing agent instead of feldspar frit in stoneware and wall tile glaze compositions was investigated. Using a standard glaze recipe, glazes with different amounts of pumice, and thus different colour, brightness and Vickers hardness values, were prepared. Their particle size distributions, thermal microscopy behaviour, dilatometer and Rietveld X-ray diffraction (XRD) results were evaluated. The formation of new phases and microstructural changes that occurred in the formulations were also investigated via XRD, scanning electron microscopy and energy-dispersive X-ray analyses. On the basis of these analyses, it was determined that, using pumice, low-cost wall tile and stoneware glaze formulations that have the required performance properties can be developed.

Keywords: Pumice, glaze, flux, wall tile, stoneware.

1. Introduction

A glaze is a glass material designed to melt onto the surface of a tile during firing and then adheres to the tile surface during cooling. Glazes can be collared or used to produce special textures, thus providing both moisture resistance and decoration. Understanding the reactions that occur on the microlevel is important for the development of glaze compositions. The raw materials used for the preparation of glazes include industrial grade silica (SiO_2), zircon (ZrSiO_4), kaolin ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$), feldspar ($\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$), dolomite ($\text{Ca} \cdot \text{Mg}(\text{CO}_3)_2$), magnesium carbonate (MgCO_3), boric acid (H_3BO_3) and potassium nitrate (KNO_3).

Feldspar is widely used as a frit in stoneware and wall tile glazes. However, the rising cost and limited reserves of feldspar have created a pressing need to find alternatives for this material in the ceramic industry. Many feldspar mines have been exhausted or can no longer economically produce this mineral. Pumice, identified as amorphous aluminium silicate, occurs as a result of volcanic activity and is a porous, spongy, volcanic, glassy rock that resists physical and chemical degradation. It is considered to be a glass because it has no crystal structure. Notably, pumice functions as a smelter in glazes in a manner similar to that of feldspar [1-5].

Therefore, the use of pumice as a fluxing agent instead of feldspar frit in stoneware and wall tile glaze compositions was investigated. Using a standard glaze recipe, glazes with different amounts of pumice, and thus different colour, brightness and Vickers hardness values, were prepared. Their particle size distributions, thermal microscopy behaviour, dilatometer and Rietveld X-ray diffraction (XRD) results were evaluated. The formation of new phases and the microstructural changes that occurred in the formulations were also investigated via XRD, scanning electron microscopy (SEM) and energy-dispersive X-ray (EDX) analyses.

2. Experimental

A standard glaze recipe was used for all evaluations (Table 1). To prepare glaze slips, each raw material was accurately weighed and charged into a ball mill along with water and appropriate additives (0.03% carboxymethyl cellulose and sodium tripolyphosphate). Milling was conducted for approximately 30 min.

Table 1. Standard glaze recipe mole ratios

Na_2O	K_2O	CaO	ZnO	Al_2O_3	SiO_2
0,0297	0,039	0,069	0,059	0,1089	0,693

After milling, the prepared glaze slips were wet sieved, and the fraction passing through a 63 micron sieve was retained for use as a glaze. The particle size distribution of the mud was determined using a laser diffraction particle size analyser.

The slips were then applied to 5 cm × 5 cm dried ceramic wall tile and stoneware bodies and fired at 1125 °C or 1200 °C in a laboratory electric furnace. A heating rate (20°C per minute) appropriate for a fast firing procedure was used.

The crystalline phases in the samples (fired, glazed tile surfaces) were identified using an X-ray diffractometer (Rigaku Rint 2000 series diffractometer) with Cu K α radiation working at 40 kV and 30 mA.

A Vickers microhardness tester with a diamond pyramid was used to measure the micro hardness of the glaze surface by applying a load of 1 kg for 10 s. The colouring parameters L*, a* and b* for all fired tiles were measured using a Minolta spectrophotometer.

The gloss of the samples was measured using a gloss metre (Minolta Gloss 268) with light incident angles on the glaze surface of 20°, 60° and 85°.

A Misura 3.32 ODHT-HSM heated microscope was used to evaluate the melting behaviour of the glazes. The microstructure and crystallinity of the glazes were inspected using a scanning electron microscope (SEM). The surfaces of the samples were chemically etched using a 5% HF solution for 30 s. The etched samples were then thoroughly washed with water and the samples were coated with a thin film of gold–palladium and examined using a CamScan S4 SEM at an accelerating voltage of 20 kV. An ultra-thin window energy dispersive x-ray spectrometer (EDX-LINK ISIS 300) attached to the SEM was also used for the chemical analysis.

3. Results and discussion

3.1 Properties of the glazes

When preparing a ceramic glaze suspension, it is necessary to ensure that the suspension has the required properties. Several parameters must be rigorously controlled, including the particle size, solids concentration and composition. The glaze samples prepared for this study different proportions of pumice (5, 10, 15, 20 and 25%) replaced by frit.

To characterize the different glazes, their particle size distribution was determined. A typical distribution profile (for sample L2) is presented in Figure 1, and the corresponding values are listed in Table 2. So many advantages of pumice additive glaze such as particle size distribution was smaller than frit glaze recipes.

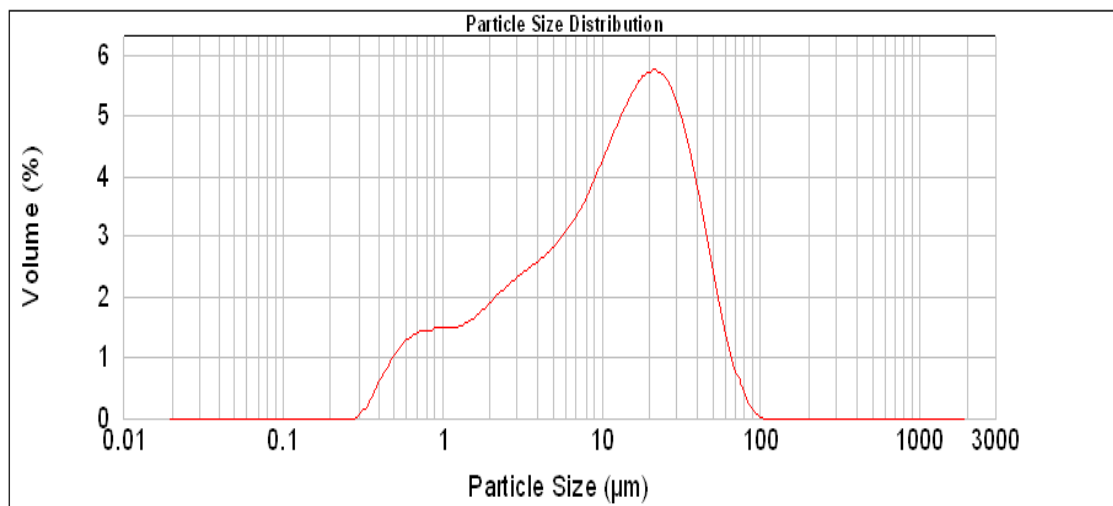


Figure 1. Particle size distribution of glaze L2

Table 2. Particle size distribution of glaze L2

Sample name	d10 (µm)	d50 (µm)	d90 (µm)
L2	1,27	12,116	38,656

3.2. Properties of the fired samples

The glazes were then carefully applied to 5 cm × 5 cm dried ceramic wall tile and stoneware bodies to obtain the correct thickness and smoothness. After glazing, the tiles were heated intensely (wall or floor tile product changed from 1125 °C to 1200 °C) to strengthen them and give them the desired porosity. In ceramics, many phases come into play: solid phase of the raw materials, liquid phase of the molten glaze matrix and glass phase of the fired, cooled glaze. Throughout the firing process, both chemical and structural changes occur, leading to changes in the phases of the material. In particular, firing causes a chemical reaction resulting in vitrification of the glaze, essentially turning it into glass [6-12].

3.3. Composition of the fired samples

Viscosity is an important property of glazes and is very sensitive to minor differences in composition, allowing for theoretical studies of the glass structure or evaluation of important glass properties, such as bubble retention, flow over ceramic bodies, quality consistency, glaze preparation and manufacturing. In particular, viscosity during firing determines the glaze flow over the ceramic body; an appropriate flow rate results in a uniform layer without draining from the surface [6]. Viscosity also determines the facility for gas bubble elimination during glaze formation. Thus, the glaze firing interval is related to the magnitude of the viscosity variation with temperature. This variation directly influences the workability and the strengthening and relaxation of glasses and glazes.

Because viscosity is sensitive to changes in the composition of glazes, the compositions of the various pumice-containing glaze formulations were evaluated using XRD analysis. The results are shown in Figure 2.

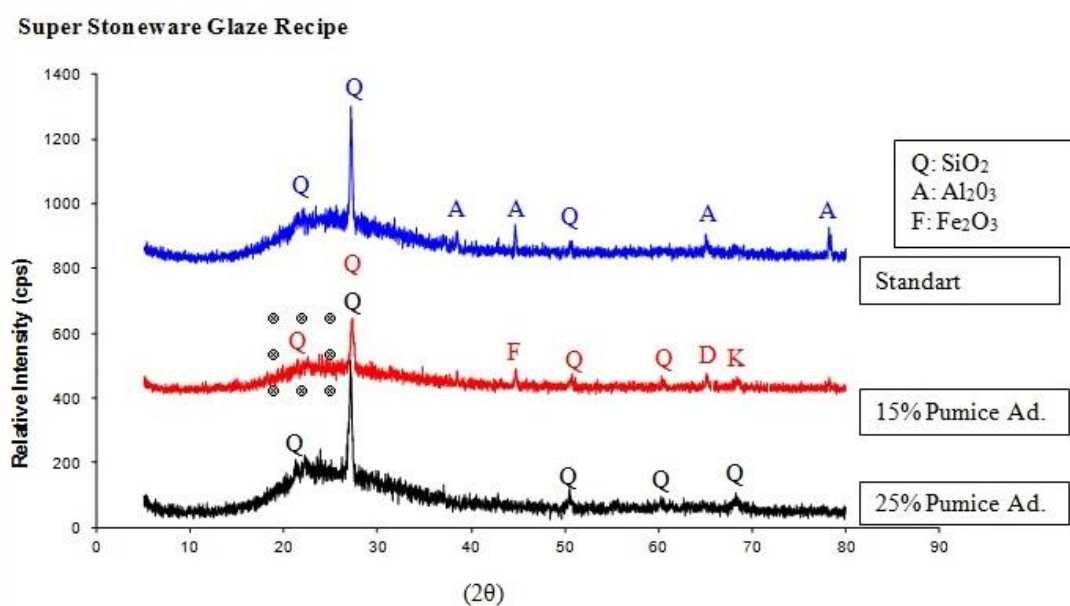


Figure 2. XRD results of fired samples.

In the XRD pattern of the Nevsehir pumice, which is considered to be an amorphous quartz, a glassy phase structure can be seen very clearly. Aim of frit mission for the conventional glaze achieved by pumice addition. The main glassy phase firstly important for the glaze structure.

3.4. Gloss of the fired samples

An important property of surface glazes is their gloss, which is related to the ability of the surface to directly reflect light. Gloss depends basically on the surface roughness and absorbance. When gloss is high, it is easy to identify surface defects (flaws); with a low surface gloss, the defects are difficult to identify and often remain hidden. The degree of surface gloss can be measured by observing the light reflection behaviour of a surface using a glossmeter [15]. Results of gloss values were change from 48.8 to 62.5 for 20°, and from 72.1 to 87.3 for 60°. So, its good results for the glaze, but colour changes effected according to Fe₂O₃ content.

Hardness of fired samples were increased according to standard glaze recipe. Increasing these values are given at Table 3.

Table.3. Hardness of fired samples

Samples	Hardness of fired samples
Standard Recipe	11,04 kgf/mm ²
5% Pumice additive glaze recipe	13,11 kgf/mm ²
10% Pumice additive glaze recipe	12,88 kgf/mm ²
15% Pumice additive glaze recipe	15,18 kgf/mm ²
20% Pumice additive glaze recipe	16,43 kgf/mm ²
25% Pumice additive glaze recipe	17,53 kgf/mm ²

Color of fired samples were not changed but slightly effect according to Fe₂O₃ impurities related values shown at Table 4.

Table.4. Hardness of fired samples

Sample Name	L	a	b
Standard Recipe	79,43	2,12	9,84
5% Pumice additive glaze recipe	78,73	2,12	11,40
10% Pumice additive glaze recipe	77,74	2,46	11,26
15% Pumice additive glaze recipe	77,40	2,29	11,82
20% Pumice additive glaze recipe	76,70	2,93	13,04
25% Pumice additive glaze recipe	76,23	2,92	11,69

3.5. Surface tension of the fired samples

Surface tension is another important property of glazes. The flow of a glaze during firing and its wettability are strongly influenced by its surface tension. Several studies have been conducted to determine the influence of surface tension on glaze formation. Glass manufacturers have, for example, analysed the influence of surface tension on reactions between glass components and the disappearance of heterogeneities in glass fluids.

A low surface tension favours the elimination of gaseous bubbles during glass melting and prevents the formation of nonhomogeneities, while a high surface tension favours the reabsorption of these bubbles during glass cooling. In a cast glaze with low surface tension, the glaze surface will be smoother, bubbles and craters will be eliminated easily, and the solid surface will be brighter; on the other hand, a very high surface tension favours the reabsorption of bubbles during cooling, causing glaze roughness (i.e. 'wrinkles').

Measuring the surface tension of a matte glaze is quite difficult because the glaze is composed of a melt and crystals. There are three major methods for measuring the surface tension of glass, including the drop-weight method, the bubble pressure method and the fibber method. The surface tension of glass can also be estimated using a heated microscope, which is more appropriate for estimation of the surface tension of a glaze. Thus, a heated microscope was used to observe the melting behaviour and estimate the surface tension of the fired glazes [17]. The results are shown in Figure 3 for sample L2. Melting behaviour of pumice recipes were achieved at lower temperature for the glaze occurrence.

3.6. Thermal expansion of the fired samples

The glaze-body interactions that occur during glost firing depend on several variables, such as the compositions of the body and the glaze, thickness of the glaze layer, peak glost firing temperature and soaking time, processing route (one or two firings), whether the glaze is fritted and to what extent, viscosity of the molten glaze and the mutual solubility of the body and glaze components [14-15].

Thermal expansion coefficients of the tile bodies and glazes were measured using a dilatometer up to 600 °C. The results are presented in Figure 4. The thermal expansion coefficients of the wall tile body and stoneware body at 400 °C were found to be $64,607 \times 10^{-7}$ and $70,381 \times 10^{-7}$, respectively, while the thermal expansion coefficients of the wall tile and stoneware glaze at 400 °C were determined to be $78,207 \times 10^{-7}$. These results were indicate that glaze structure was responsive according to standard recipe.

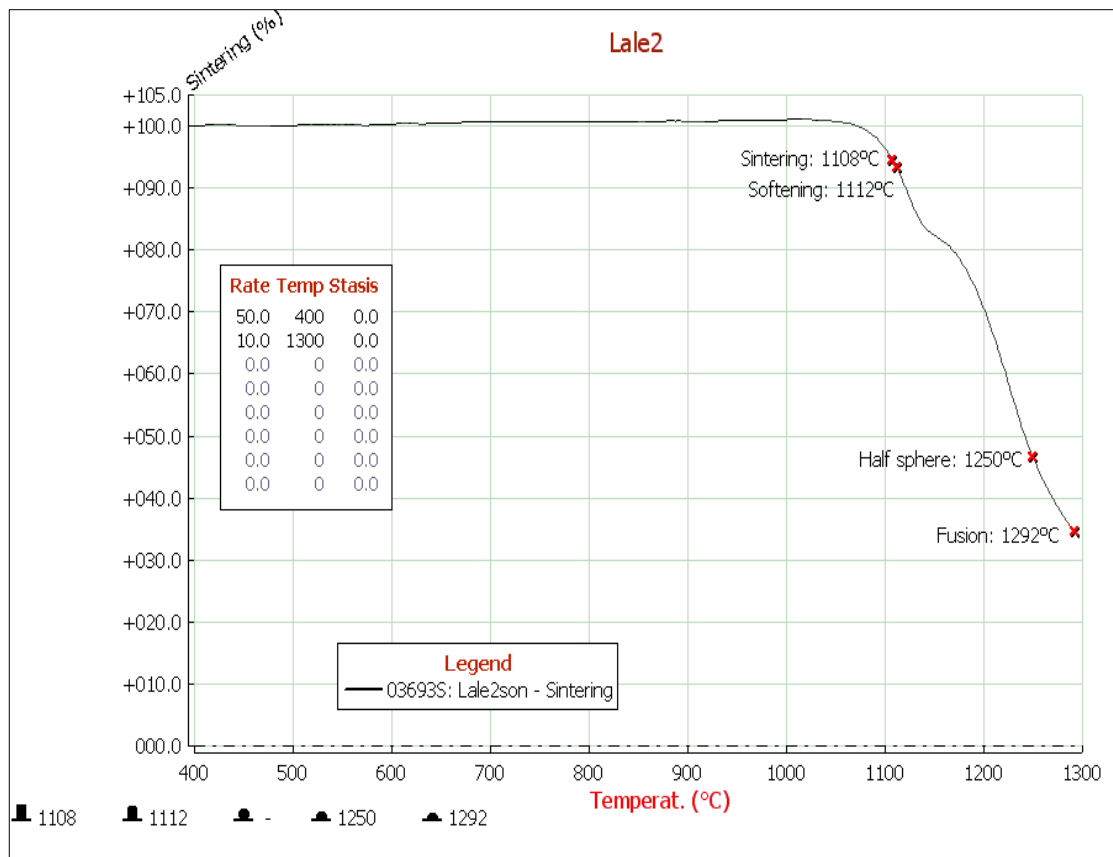
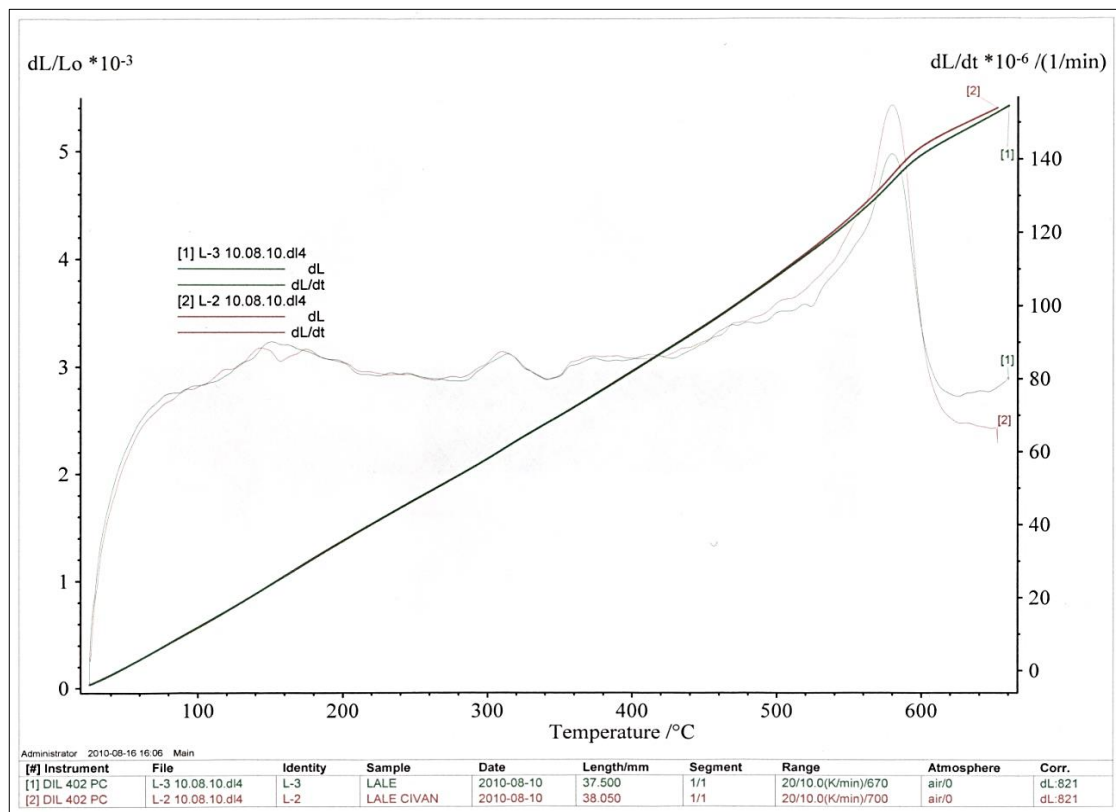


Figure 3. Melting behaviour of sample L2.



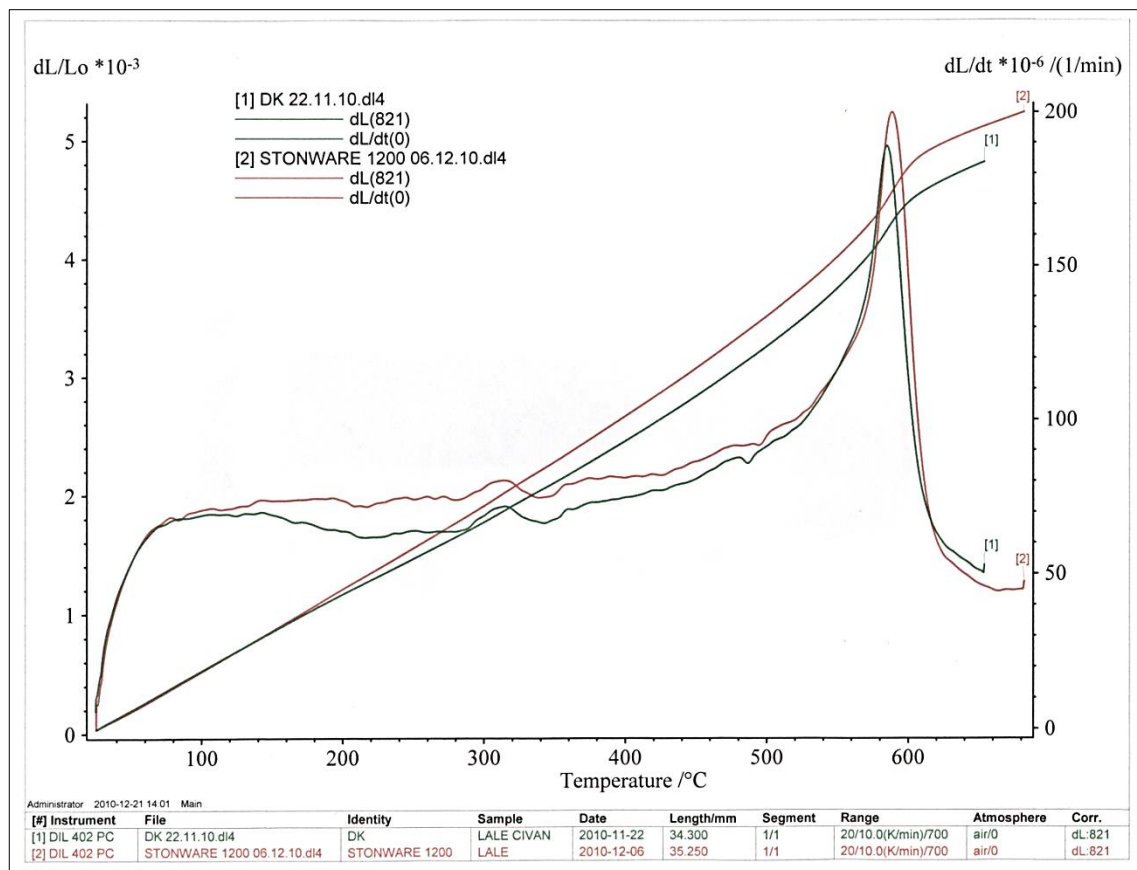


Figure 4. Dilatometer results for the various fired samples.

Morphology of fired samples commonly glassy phase and crystalline phase, small amount of porosity was observed shown as Figure 5. With pumice additive glaze due to forming dispersed crystal particles (quartz and cristobalite) in the glass matrix.

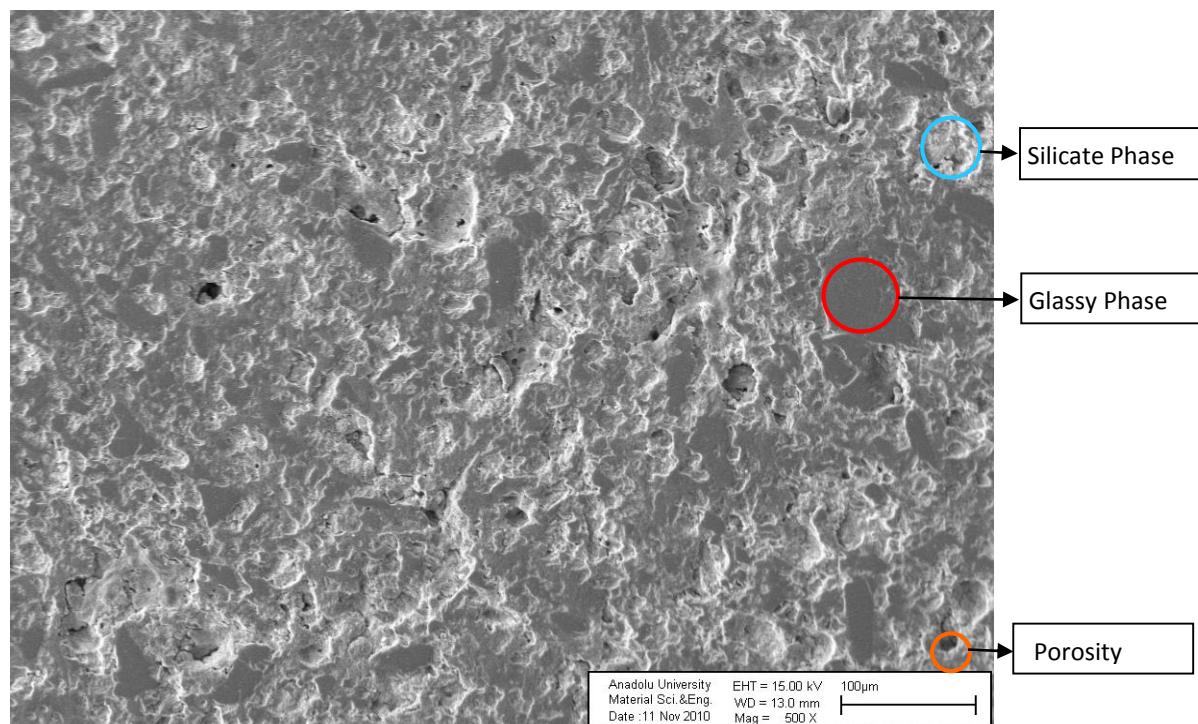


Figure 5. SEM results of fired sample (5% pumice additive sample).

EDX spectrum of glaze sample with pumice, melting feldspar and pumice in the original compositions was silicate structure, the glassy areas were obtained. One of obtained glassy areas are determined in Figure 6.

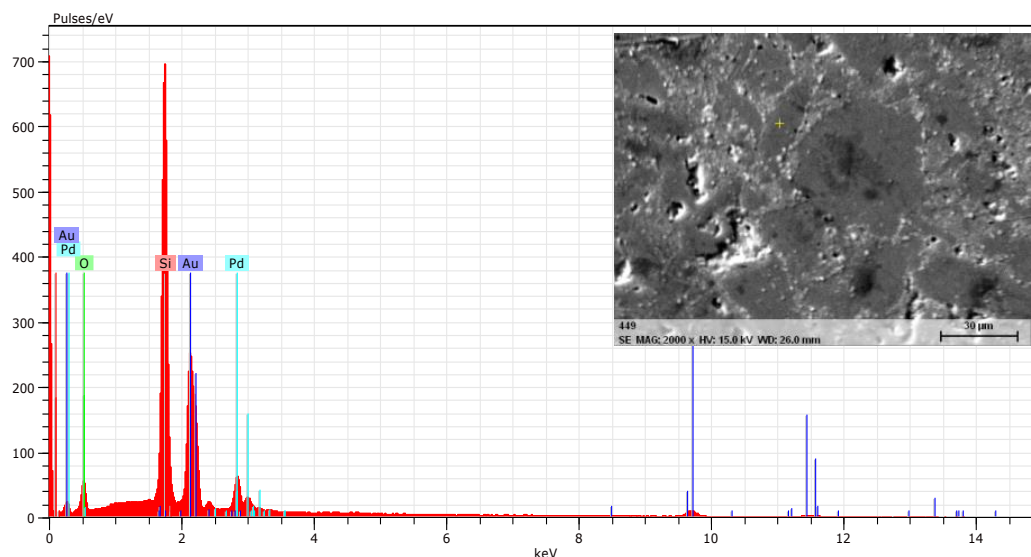


Figure 6. Element analysis (EDX) of the fired samples.

Importantly, the results of the EDX analysis are in good agreement with the results of the XRD analysis.

4. Conclusion

In results, XRD of pumice called amorphous quartz the glassy phase structure is seen clearly, so instead of feldspar created standard glaze recipe by the addition of different proportions of pumice recipe can be possible to use according to glaze standards.

From this study, it can be concluded that, by using pumice, wall tile and stoneware glaze formulations can be developed with the required performance properties at low cost.

5. Suggestions

In this study, wall tile and stoneware glaze receipt with pumice additive were developed according to industrial applications because of the energy save and lower pumice cost.

References

- [1] C. Leonelli, T. Manfredini, C. ve Siligardi, *Int. Cer. J.*, April (2002), 31–35.
- [2] C.F. Mingarro, “Invited conference,” in: *The Proceedings of the Congress Qualicer*, Castellon, Spain, March (1994).
- [3] E.V. Henkes, Y.G. Onodo, M.W. ve Carty, *Science of White wares*, Wiley-American Ceramic Society, 1996, pp. 358–359.
- [4] K. Shaw, *Ceramic Glazes*, Applied Science, Elsevier Pub., London, 1971.
- [5] A. Ibanez, P. Pena, F. Sandoval, J.M. Gonzalez, *Am. Ceram. Soc. Bull.*, 71 11 (1992) 1661–1668.
- [6] K.G. Fugmann, H. Reh, *How to Produce Tiles*, Interceram, 1992, pp. 1–13.
- [7] A. Brusa, A. Bresciani, *Am. Ceram. Soc. Bull.*, 74 9 (1995).
- [8] E. Sanchez, J. Garcia, V. Sanz, E. Ochandio, *Tile Brick Inter.*, 6 4 (1990) 15–21.
- [9] C.D. Fuante, Queralt, I.mat, T. Sanfeliu, *Tile Brick Inter.*, 6 4 (1990) 21–23.
- [10] J.S. Reed, *Introduction to The Principles of Ceramic Processing*, New York State College of Ceramics, Alfred University, New York, 1989.
- [11] A. Escardino, *Tile Brick Inter.*, 9 2 (1993) 73–77.



- [12] K.G. Fugmann, H. Reh, *Interceram*, (1992) 1–13.
- [13] A. Goleanu, *Key Eng. Mater.*, 264 (2004) 264–268.
- [14] F.J. Torres, J. Alarcon, *J. Europ. Ceram. Soc.*, 25 4 (2005) 349–355.
- [15] R.A. Eppler, D.R. Ve Eppler, *Ceram. Eng. Sci. Proc.*, 16 (1995) 40–45.
- [16] M. Liu, J. Takagi, A. Tsukuda, *J. Mater. Proc. Tech.* 145 3 (2003) 276–280.
- [17] B. Burzacchini, M. Paganelli, G.H. Christ, *Ceram. Eng. Sci. Proc.* 17 1 (1996), 60–66.