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The use of pumice (pumicite) in transparent roof tile glaze composition

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Abstract

In this study, the use of pumice as an alternative fluxing agent instead of Na-Feldspar in the transparent roof tile glaze composition was investigated. The experiments were designed as a mixture experiment. According to heating microscope results, pumice was observed deforming at 850 °C and flowing at 1270 °C. Considering the properties of the pumice it is possible to use it in raw glaze (without using frit) applications instead of feldspar. Colour, brightness and hardness values of fired samples were measured. These data were analysed with MINITAB 13.0 statistical software programme. Microstructure of glaze/tile interfaces of single fired samples was studied by using a scanning electron microscope (SEM). The use of pumice in the glaze composition showed no negative effect on the colour, brightness and hardness values and decreased the flowing temperature of the glaze. It was concluded that pumice could easily replace Na-Feldspar as an alternative fluxing agent in appropriate proportions in such kind of a roof tile glaze composition without causing undesired consequences.

Keywords: Mixture experiment design; Traditional ceramics; Colour; Hardness

1. Introduction

In recent years, roof tile industry focused on giving the tiles shiny decorative and aesthetical appearances, improving mechanical strength and resistance to atmospheric conditions. Under the lights of developing technologies and new trends it has been thought that it is time for the relevant sector to have its own alternatives and varieties. Therefore, the market offers numerous types of roofing tiles (engobed or glazed) for covering pitched roofs.[1] Glazed roof tiles are being extensively used in some European countries, in the Far East countries like China and Japan, and also in the United States. There have been different studies conducted on glazing of bricks and roof tiles.[2–4]

Pumice (pumicite) is a light-coloured natural sponge-like material of volcanic origin composed principally of high silica, low iron and magnesium content. In particular, it is found in the Mediterranean area (Italy, Turkey, Greece and Spain). Worldwide, over 50 countries produce pumice products.[5] Pumice is used in many applications such as in the chemical, dental, cosmetic, abrasives, cement, concrete, ceramic and glass industries because of being an inexpensive and widespread geological raw material. However, the most usage of pumice is in the construction industry. Pumice has been used in cement and as an aggregate in the production of lightweight concrete (LWC) in many countries of the world. There have been also some studies concerning production of LWC with the use of pumice.[6–9] Pumice has the potential to be used as a ceramic raw material.[10–12]

Feldspatic minerals have long been universally used in ceramic glaze formulations for their fluxing power.[13] Due to running out of natural feldspar resources, many researches were started to investigate alternative fluxing agents that can replace feldspar. In this study, transparent glaze composition that has low melting temperature and compatible with the roof tile body was developed. And then, the use of pumice in the transparent roof tile glaze composition as an alternative fluxing agent instead of sodium feldspar was investigated. Mixture design is used to identify components proportions to optimum response. The component proportions are non-negative and, if expressed as fractions of the mixture, they sum to unity.[14] Thus, if the number of components in the

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Table 1
Chemical compositions of raw materials and pumice used in transparent glaze composition (in wt.%)

Raw material	Oxides (in wt.%)									
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	B_2O_3	L.O.I.[a]
Kaolin	71.15	17.95	0.56	0.98	0.70	1.56	0.32	0.40	–	6.38
Ulexite	3	–	0.05	–	17	–	5.50	–	39	33.45
Na-Feldspar	70	18.30	0.05	0.05	0.40	0.10	9.77	0.25	–	0.40
Pumice	61.47	17.50	2.26	0.16	4.25	1.70	6.80	5.12	–	0.74

[a] L.O.I.: loss on ignition.

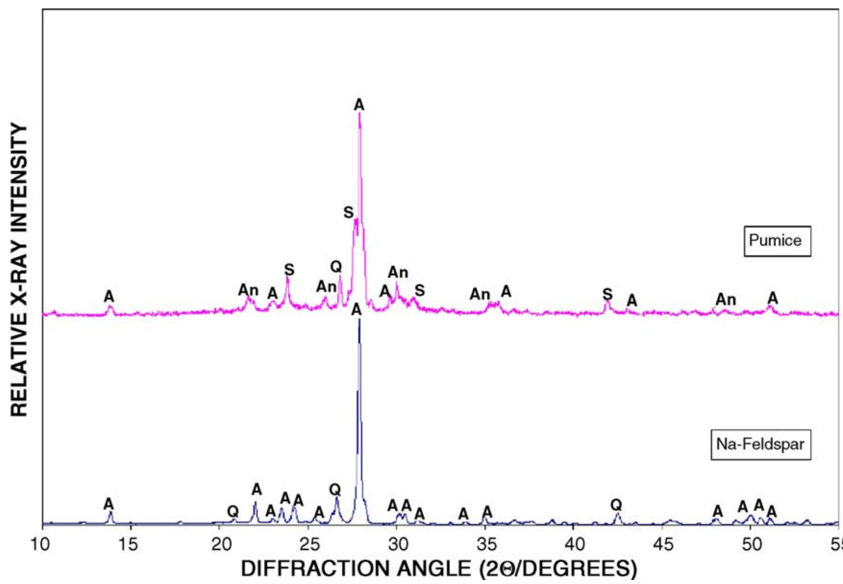

Fig. 1. XRD pattern of the pumice and Na-Feldspar (A: albite, An: anorthoclase, S: sanidine, Q: quartz).

system is denoted by q and if the proportion of the ith component in the mixture is represented by x_i, then,

$$x_i \geq 0; \quad i = 1, 2, 3, \ldots, q$$

and

$$\sum_{i=1}^{q} x_i = x_1 + x_2 + \cdots + x_q = 1, 0. \tag{1}$$

2. Experimental procedure

Kaolin, ulexite and sodium feldspar (Na-Feldspar) were used as raw materials in the transparent glaze composition. Pumice obtained from Isparta region of Turkey was also used as an alternative fluxing agent instead of Na-Feldspar in the recipe. Chemical analysis results of these raw materials and pumice are given in Table 1. Pumice and the other raw materials were ground in a laboratory-scale ball mill for reducing the particle size. X-ray diffraction analysis results were determined by Rigaku (Ragaiw-ring-2000) X-ray diffractometer. XRD patterns of the Na-Feldspar and pumice are shown in Fig. 1. Heating microscope results received from the Leica heating microscope of Na-Feldspar and pumice are given in Fig. 2. According to Fig. 2, pumice was observed to start deforming at about 850 °C and flowing at about 1270 °C while Na-Feldspar started deforming at about 1100 °C and flowing at about 1380 °C. Also, it was observed that pumice melts at lower temperature compared to Na-Feldspar. Roof tile sludge which consists of kaolin, quartz and feldspar were taken from a commercial company in Eskisehir. After drying and grinding the sludge, the granulated powders with moisture of 5–6% were pressed under 200 kg/cm^2 pressure to prepare 10 cm × 20 cm dimension tiles. Transparent glaze

Table 2
Characteristic temperatures of standard (TP-0) and 100% pumice containing (TP-100) glazes

Recipe	Characteristic temperatures (°C)					
	Start of deformation	Deformation range	Sphere formation	Hemisphere formation	Flow range	Flow
TP-0	697	697–880	862	880	880–893	893
TP-100	372	372–879	799	879	879–881	881

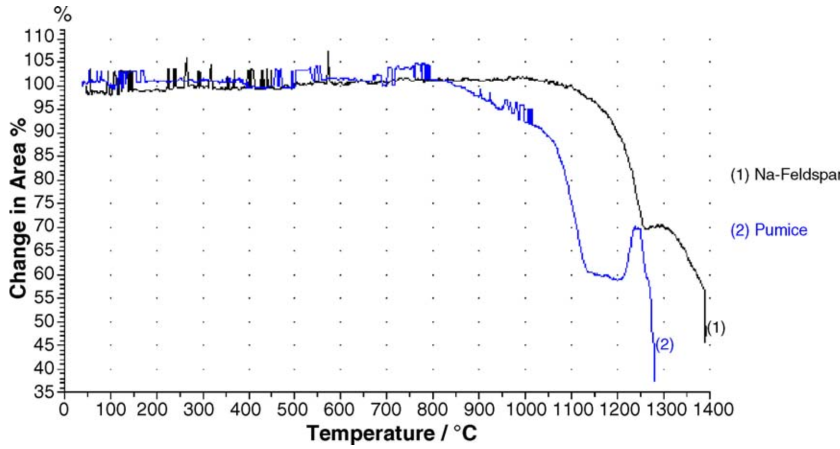

Fig. 2. Graph of change in area % vs. temperature of Na-Feldspar and pumice.

composition compatible with commercial roof tile body having low melting temperature was developed (TP-0, without pumice addition) and then pumice was added into the glaze recipe replacing Na-Feldspar at certain proportions in wt.%; 25% (TP-25), 50% (TP-50), 75% (TP-75) and 100% (TP-100). Synthesized new glaze batches were charged into alumina ball jet-mills and wet-ground for 1 h. Melting behaviour of the produced glazes was determined by Leica heating microscope. The prepared glazes were screened by 100 mesh (100 μm) sieves and then under sieve portions were applied direct on to the unfired green tiles by spraying technique. After having been dried in a furnace at 105 °C for 1 h, glazed tiles were single fired in a laboratory type Nabertherm brand electrically heated furnace at 950 °C for 4 h. The experiments were designed as a mixture design. It was used to evaluate the colour, brightness and hardness. Five samples were prepared for each glaze recipe and also five measurements were done for each sample. Colouring parameters of all samples were determined by Minolta CM-3600d model spectrophotometer and the results were expressed in L^*, a^*, b^* values. Brightness values of glazed samples were obtained with Minolta Multi-Gloss 268 model gloss-meter. Hardness tests of the glazed surfaces were measured by Shimadzu HMV-2000 model micro-hardness equipment (load = 100 g, time = 10 s). Colour, brightness and hardness data were analysed with MINITAB 13.0 statistical software programme. Microstructure of glaze/tile interfaces of fired samples was investigated by using a Camscan S4 series scanning electron microscope (SEM). And also quantitative analysis of the glaze and the interface was carried out by using SEM with an energy dispersive X-ray spectrometer (EDX-LINK ISIS 300).

3. Results and discussions

Heating microscope analysis results of standard TP-0 and TP-100 glazes are shown in Table 2. When the analysis results observed, it has been seen that the starting deformation temperature of 100% pumice containing glazes (TP-100) is 372 °C while the starting deformation temperature of glazes containing 100% feldspar (TP-0) is 697 °C. Hence, this is approximately half of the TP-0 glaze. Also it can be seen that the temperatures of both hemisphere formation and flow range of TP-0 and TP-100 glazes are similar. These results express that there will be no change at the melting behaviour of the glaze by using pumice instead of feldspar in the glaze composition.

Mean values of colour, brightness and micro hardness of glazed samples are shown respectively in Tables 3–5. Analyses of regressions for mixtures that have been obtained from MINITAB 13.0 statistical software programme are also

Table 3
Colour measurement results of glazed samples

Sample	L^* (mean values)	a^* (mean values)	b^* (mean values)
TP-0	32.25	6.97	6.95
TP-25	33.70	8.02	8.63
TP-50	32.99	7.48	7.82
TP-75	33.15	8.16	7.99
TP-100	32.54	7.78	9.53

Table 4
Brightness test results

Sample	Brightness mean values (for 20°)
TP-0	44.7
TP-25	49.8
TP-50	50.2
TP-75	52.1
TP-100	49.2

Table 5
Micro-hardness test results

Sample	Micro-hardness mean values (MPa)
TP-0	359
TP-25	398
TP-50	417
TP-75	392
TP-100	381

Table 6
The results of regression coefficients analysis for a^*

Estimated regression coefficients for a^* (component proportions)					
Term	Coef	SE Coef	*T*	*P*	VIF
Na-Feldspar	7.002	0.07877	*	*	1.563
Pumice	7.816	0.07877	*	*	1.563
Na-Feldspar*Pumice*(-)	3.013	0.72763	4.14	0.000	1.250
Na-Feldspar*Pumice*(-)2	14.300	1.68039	8.51	0.000	1.667
S = 0.19294	PRESS = 1.1090				
R-Sq = 84.96%	*R*-Sq (pred) = 78.66%	*R*-Sq (adj) = 82.81%			

Table 7
The results of regression coefficients analysis for brightness

Estimated regression coefficients for brightness (component proportions)					
Term	Coef	SE Coef	*T*	*P*	VIF
Na-Feldspar	44.87	0.5867	*	*	1.661
Pumice	49.38	0.5867	*	*	1.661
Na-Feldspar*Pumice	16.41	2.6659	6.16	0.000	2.429
S = 1.3941	PRESS = 56.714				
R-Sq = 76.25%	*R*-Sq (pred) = 68.50%	*R*-Sq (adj) = 74.09			

shown below in the text. There are not any visible changes in the colour of the samples. Since the glaze, which has been used in this study, is transparent, it makes the body appear red. For this reason only a^* value has been considered in the colour analysis. Mixture design has two components; Na-Feldspar (x_1) and pumice (x_2). a^* data ($\hat{y}$) is the response. The experiment has been designed and analyzed as a Simplex Centroid Design with two components and two design degrees. A fitted full quarticle model which represents a^* value has been found as following:

$$\hat{y}(a^*) = 7.002x_1 + 7.816x_2 + 3.013(x_1x_2)^{-1} + 14.3(x_1x_2)^{-2}. \quad (2)$$

Analyses of regressions for mixtures (a^* versus Na-Feldspar; pumice) are given in Table 6. Fitted model is reflected in the high value of *R*-Sq (adj) = 82.81%. Fig. 3 shows that approximately 88% pumice containing glaze has the maximum a^* and this value is $\hat{y} = 8.35$.

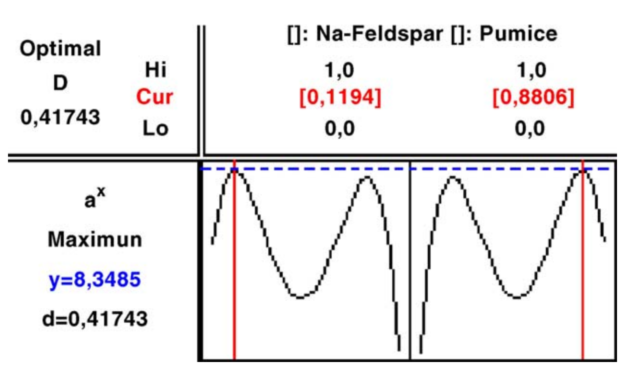

Fig. 3. The fitted model plot for a^* value.

Same mixture design and analysis were done for brightness. A fitted full quadratic model which represents brightness value has been found as following:

$$\hat{y}\,(\text{brightness}) = 44.87x_1 + 49.38x_2 + 16.41(x_1x_2). \quad (3)$$

The results of regression coefficients analysis of brightness (versus Na-Feldspar; pumice) are given in Table 7. The fitted quadratic model is reflected in the high value of *R*-Sq (adj) = 74.091%. Approximately 64% pumice containing glaze has the maximum brightness and this value is $\hat{y}$ (brightness) = 51.54.

Same operations were done for micro hardness. A fitted full quadratic model which represents micro-hardness value has been found as following:

$$\hat{y}\,(\text{micro-hardness}) = 361.2x_1 + 376.4x_2 + 164.6(x_1x_2). \quad (4)$$

Micro-hardness (versus Na-Feldspar; pumice) results are given in Table 8. The fitted quadratic model is reflected in the high value of *R*-sq (adj) = 66.16%. Fifty percent pumice containing glaze has the maximum micro-hardness and this value is $\hat{y}$ (micro-hardness) = 409.97 MPa.

Microstructure investigations that were done on the representative polished cross section samples showed that an interaction layer occurs at the interfaces of all samples. Fig. 4 shows the images of backscattered electron microscope (BSE) of glaze/tile interface belonging to glazed roof tile samples. It is seen clearly that if the pumice amount in the glaze increases, the thickness of the interface interaction layer decreases. Also, it has been found from EDX results that chemical compositions of both glaze and interface layers of the samples were different. Highest Al_2O_3 and SiO_2 amounts have been obtained in the glaze of TP-50 sample

Table 8
The results of regression coefficients analysis for micro-hardness

Estimated regression coefficients for micro-hardness (component proportions)					
Term	Coef	SE Coef	*T*	*P*	VIF
Na-Feldspar	361.2	5.424	*	*	1.661
Pumice	376.4	5.424	*	*	1.661
Na-Feldspar*Pumice	164.6	24.647	6.68	0.000	2.429
$S = 12.888$	PRESS = 4771.7				
R-Sq = 68.98%	R-Sq (pred) = 59.50%	R-Sq (adj) = 66.16%			

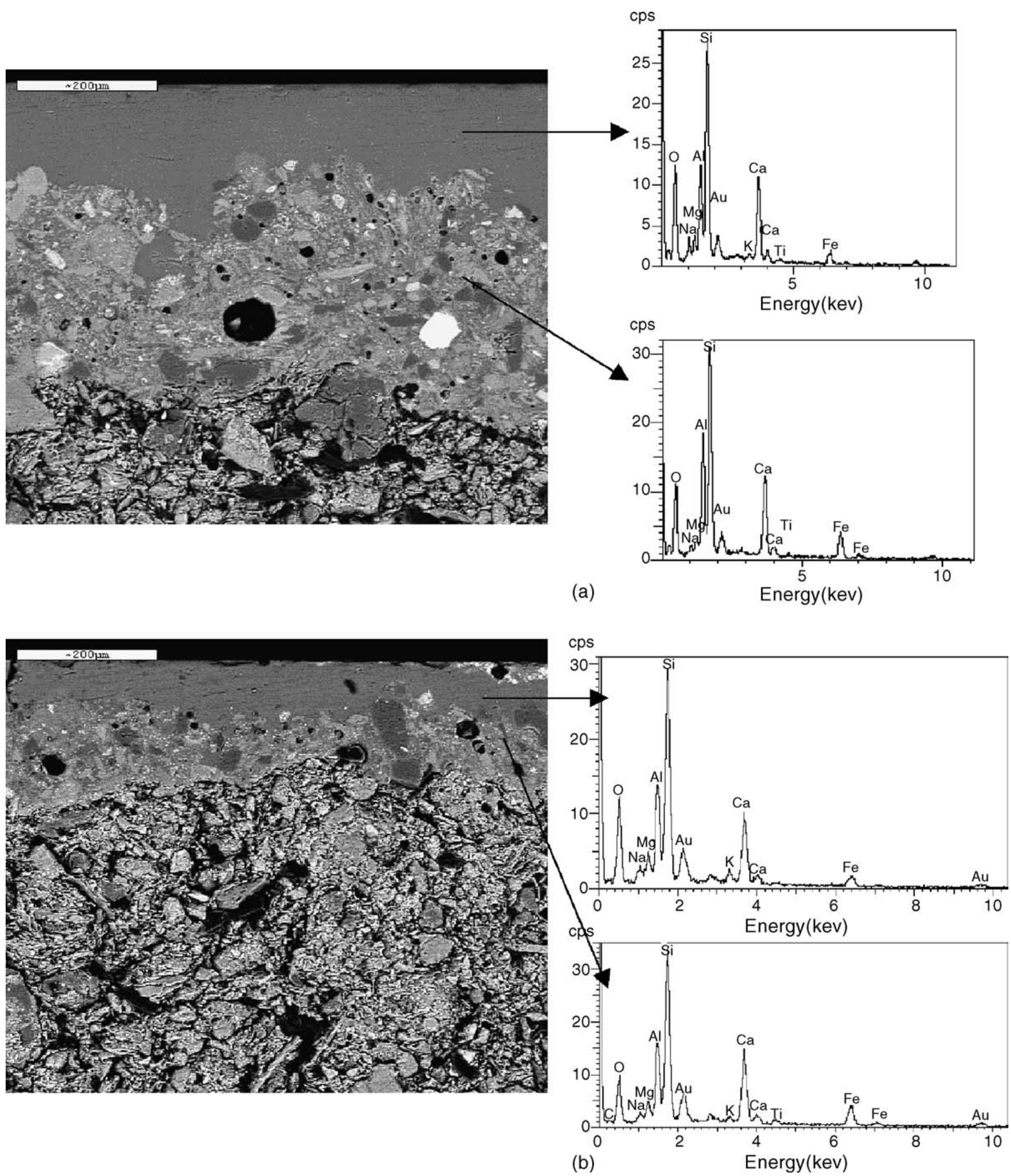

Fig. 4. Back scattered electron (BE) SEM image of the glaze (on the top), interface (in the middle) and conventional roof tile body (at the bottom). EDX analysis results of glazes and interfaces are also shown (a) TP-0, (b) TP-100.

that has the highest hardness value. This is compatible with the results of hardness regression analysis.

4. Conclusion

The experimental results showed that the use of pumice in the glaze composition does not have any negative effect on the colour, brightness and hardness values and decreases the melting temperature of the glaze. Because of being an inexpensive raw material, it is expected that the usage of pumice reduces the cost of the glaze. As a result, it was concluded that pumice could easily replace Na-Feldspar as an alternative fluxing agent in appropriate proportions in such kind of a roof tile glaze composition without causing undesired consequences.

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