THE FLOTATION ENRICHMENT OF WESTERN ANATOLIAN KAOLIN TO BE USED IN PORCELAIN BODIES AND ENGOBES

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ABSTRACT

Kaolin is one of the most important raw materials used in the ceramic industry. The desired firing color of kaolin used in porcelain tile body and engobe recipes is white with L values between 94 and 95. In a typical porcelain ceramics raw material composition the amounts of allowed impurities and components may vary. While the limiting value for Fe_2O_3+TiO_2 total content is 0.7%, SO_3 content should be less than 0.7%, Al_2O_3 min 21–23%. Western Anatolian kaolins meet most of these specifications yet their SO_3 content is way over the limit. Therefore, those kaolin raw materials cannot be directly used in the ceramics industry. The objective of this study is to investigate the use of western Anatolian kaolins, containing high amounts of alunite, in porcelain body and engobes by enriching them, implementing the flotation method. In this research, the effects of flotation parameters such as particle size, the solid ratio in pulp and the type and dosages of reagents were investigated. After the flotation process, the firing properties of enriched kaolin were examined and its physical properties such as shrinkage (%), water absorption (%) and color features expressed as L, a, b were measured. As a result of the studies, it was revealed that the enriched Western Anatolian kaolins can be used in porcelain body and engobes.

INTRODUCTION

Kaolin is a clay group, the main mineral of which is kaolinite, formed as a result of in situ decomposition of granite and other igneous/volcanic rocks [1]. Kaolinite is one of the most common clay minerals of the kaolin group and important raw materials of the ceramic industry. In general terms, kaolin is defined with the ideal composition of 46.5% SiO_2, 39.5% Al_2O_3 and 14% H_2O mainly in the form of aluminum hydrosilicate ($2H_2O.Al_2O_3.2SO_2$). In case the amount of aluminum oxide in the ideal composition decreases, iron, sulfur, and potassium enter the composition, albeit in small amounts. As a result of potassium entering the structure, the presence of alunite is detected in the ore.

Alunite is a distinctive mineral of hydrothermal kaolins, whose structure is defined as aqueous potassium aluminum silicate with a high content of sulfur trioxide (SO_3) and aluminum oxide (Al_2O_3), with a mineral form of $K_2O.3Al_2O_3.4SO_3.6H_2O$ [2-3] During the formation of hydrothermal kaolins under acidic conditions through the reaction of SO_4^{2-}-bearing solutions with volcanic glass and feldspar in volcanic rocks, when the pH of the solution reaches 4.5, kaolinite precipitates with or without alunite [2]. The presence of alunite is explained with the availability of S in the environment during formation of kaolin. During the dissolution of Feldspar (K Feldspar) minerals, K^+ will be largely removed from the environment, while some potassium will remain behind. While kaolin is formed, the presence of S and K combines with K and $Al_2(SO_3)_3$ to constitute alunite [4].

At temperatures higher than 500°C, alunite transforms into dehydrated potassium while forming highly reactive alumina via the following reaction:

$$KAl_3(SO_4)_2(OH)_6 \longrightarrow KAl(SO_4)_2 + Al_2O_3 + 3H_2O$$

At temperatures higher than 750°C, desulphation occurs through different steps, producing potassium oxide and gaseous SO_3 which is damaging for furnace refractories [5]. Aside from damaging kilns, it pollutes the environment and lead to pinholes on the surface of the ceramic products [6-7].

Furthermore, the presence of alunite has a negative effect on the rheological properties of slips, leading to disintegration after drying, and causes an increase in fire loss during the heat treatment process in ceramic production which results in irreversible degradation in the ceramic body. All these issues render alunite-bearing raw materials unsuitable for ceramic applications [7].

The aim of this work is to investigate the possible use of Western Anatolian kaolins for porcelain bodies and engobes by lowering their SO_3 content via the flotation method.

MATERIALS AND METHODS

Chemical analysis of kaolins was carried out with a Panalytical Axios XRF instrument. A PANalytical X'Pert Pro MPD X-ray diffractometer (XRD) with CuKα radiation 45 kV and 40 mA was used to identify the crystalline phases. Physical properties, linear shrinkage, water absorption, color (L, a, b) of both enriched and Ukrainian kaolins were investigated. Thermal analyses were performed with a Setaram Labsys EVO DTA – TG – DSC instrument.

The flotation method was used to reduce the SO_3 content of the kaolins used in this study. The flotation cell in which the flotation experiments were carried out is given in the Figure 1. In the experiments, a type of unsaturated fatty acid was used as the collector, and a type of alcohol-based chemical was used as the foaming agent. In order to recover the valuable mineral (kaolin) in the waste, scavenging flotation was performed after the flotation cycle. The enrichment flow chart of kaolins is shown in Figure 2.

In the first stage of the study, porcelain body compositions were created by using enriched kaolins instead of Ukrainian kaolins in certain proportions. The developed body composition recipes were referenced STDB1 (for the standard recipe), B1.1 and B1.2 for the porcelain tile. After the body composition recipes were designed, round tablets of these compositions with a diameter of 5 cm were formed and fired in certain stages. The process, which takes place in the laboratory environment, consists of grinding, clay blunging, mixing, drying, granulation, pressing, drying, and then sintering in industrial rapid-firing roller furnaces. After that, the physical properties, linear shrinkage, water absorption, and color (L, a, b) of the fired porcelain bodies were investigated. In addition, the thermal expansion behaviors of the fired bodies were determined with the DTA – TG – DSC instrument. In addition, the sintering behaviors of the body compositions were studied with a hot stage optical microscope (MISURA, Expert System Solutions, Italy) by using a fast heating rate of 50 °C/min., similar to industrial firing conditions. SEM-EDX analysis of standard porcelain bodies and second group recipes was performed with a ZEISS SUPRA 50VP SEM using the secondary electron imaging mode.

In the second stage of the study, porcelain engobe composition studies were carried out with enriched kaolins. The developed engobe composition recipes were referenced STDE1 (for the standard recipe), E1.1, E1.2, E1.3 and E1.4 for the porcelain tile. The procedure, which takes place in the laboratory environment, consists of grinding, glaze application, drying and then sintering in industrial rapid-firing roller furnaces. The engobe slips were applied on tiles by an applicator with an opening of 0.5 mm. Afterwards, color (L, a, b), brightness and the surface properties of the engobes were examined. To determine the physical properties of the engobe (linear shrinkage (%), water absorption (%), color (L, a, b)), round tablets were formed and fired in the same way as in the body compositions described above. The thermal expansion and sintering behaviors of the developed engobe compositions were also investigated.

Figure 1: *Flotation cell where flotation experiments are carried out.*

RESULTS AND DISCUSSION

1) PROPERTIES OF ENRICHED KAOLINS

The kaolins used in this study were obtained from Balıkesir – Turkey (Kaolin 1) and Aksaray – Turkey (Kaolin 2). The kaolins were enriched by the flotation method and their SO_3 contents were reduced from 2.41% to 0.8% for Kaolin 1 and from 4.50% to 1.20% for Kaolin 2. The chemical compositions of the enriched kaolins and Ukrainian kaolin used in porcelain body and engobes are given in Table 1. As shown in the table, Kaolin 1 has an Al_2O_3 content of 16.95%, SiO_2 content of 74.69%; Kaolin 2 has an Al_2O_3 content of 22.06%, SiO_2 content of 65.63%, and Ukrainian kaolin's Al_2O_3 content is 22.68% and SiO_2 content is 67.52%.

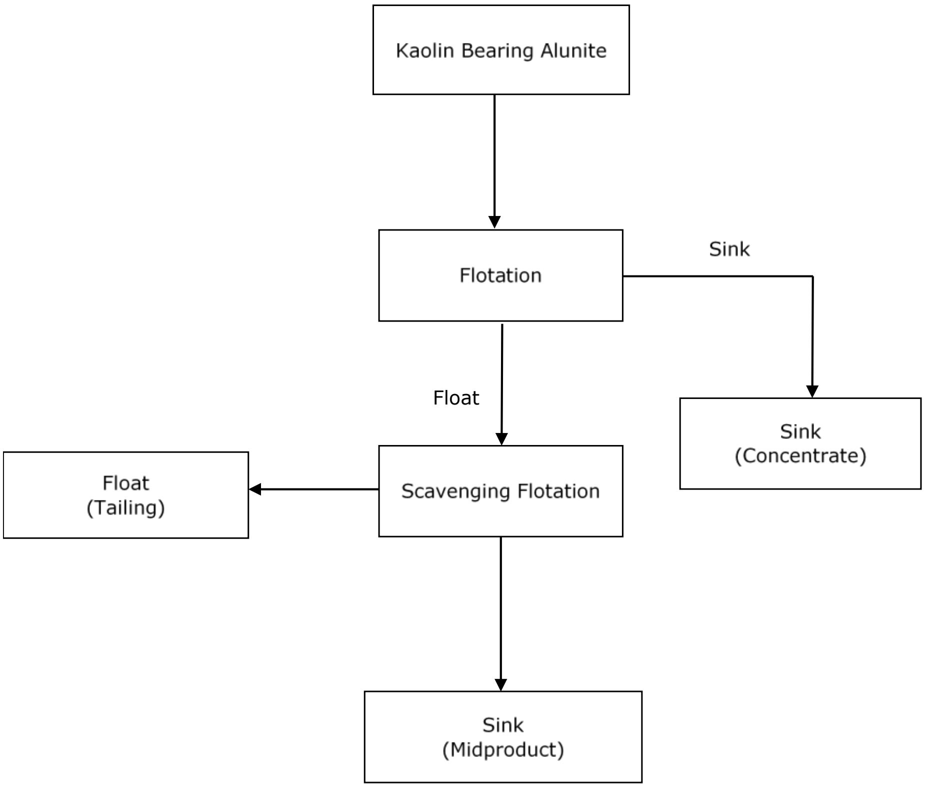


Figure 2: *Flow chart of kaolin enrichment by the flotation method.*

Materials	L.O.I.	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	MgO	Na_2O	K_2O	Total	SO_3
Kaolin 1	6.97	74.69	16.95	0.51	0.17	TRACE	TRACE	0.16	TRACE	99.45	0.80
Kaolin 2	9.20	65.63	22.06	0.44	0.16	0.15	0.07	0.09	0.84	98.64	1.20
Ukrainian Kaolin	8.07	67.52	22.68	0.51	0.20	0.26	0.08	0.09	0.48	99.89	-

Table 1: *Chemical compositions of the kaolins*

In Figure 3, XRD patterns of enriched kaolins and Ukrainian kaolin are depicted. Although the main phases in all three kaolins are kaolinite and quartz, Kaolin 1 and 2 also contain alunite phases.

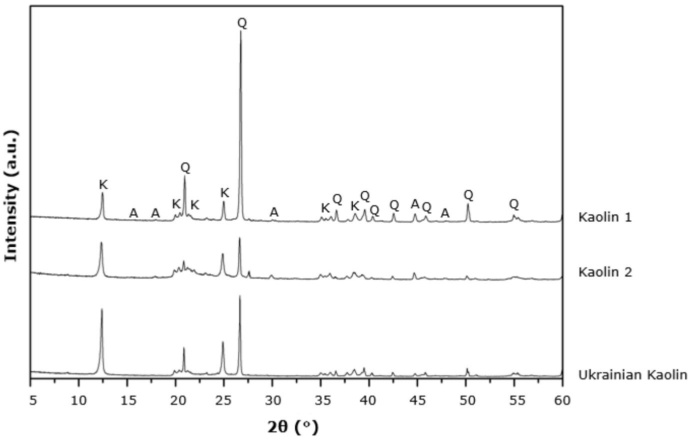


Figure 3: *XRD diffractogram of the kaolins (Q: Quartz, K: Kaolinite, A: Alunite)*

Physical and Thermal Properties			**Kaolin1**	**Kaolin 2**	**Ukrainian Kaolin**
Max. Firing Temperature		^{0}C	1205	1205	1205
Firing Time		min.	61	61	61
Size		mm	50.55	48.04	49.92
Firing Shrinkage		%	-0.60	4.40	0.66
Water Absorption		%	22.34	24.59	16,62
Color	L	-	92.69	95.43	94.27
	a	-	1.30	0.46	0.60
	b	-	2.74	3.50	3.51
Coefficient of Thermal Expansion	α_{300} °C x 10^{-7}	K^{-1}	80.66	60.26	53.52
	α_{400} °C x 10^{-7}		86.22	57.41	55.57
	α_{500} °C x 10^{-7}		94.82	55.99	58.88
	α_{600} °C x 10^{-7}		12.85	60.00	77.38

Table 2: *Physical and Thermal Properties of Kaolins*

The physical and thermal properties of the kaolins used in the porcelain body and engobes are given in Table 2. Kaolin samples were sintered according to the porcelain firing regime. The L values of the enriched Kaolin 2 is approximately 1.2 points higher than that of standard Ukrainian Kaolin. The L whiteness value of Kaolin 1 which demonstrates high thermal expansion behavior is approximately 1.5 points lower.

2) PHYSICAL AND THERMAL PROPERTIES OF DEVELOPED PORCELAIN BODIES

The variation of water absorption and firing shrinkage according to the ratios of Kaolin 1 and Kaolin 2 in the body composition is given in Table 3. For B1.1 composition, in which Kaolin 2 is used instead of Ukrainian kaolin, values of firing shrinkage of 9.01%, water absorption of 0.04% and color (L value) 83.16 were obtained. For B1.2, in which Kaolin 1 and Kaolin 2 were used instead of Ukrainian kaolin with the same ratios, the firing shrinkage was 8.42%, water absorption was 0.93%, and color L was 82.67. For standard composition (STDB1), these values are 7.50% for shrinkage, 0% for water absorption, and 81.55 for color (L). It was observed that the thermal expansion coefficient (α_{400}) values of the compositions (B1.1 and B1.2) in which floated kaolins were used, increased compared to the standard composition. This high coefficient of thermal expansion can be explained by the high silica content of Kaolin 1 used in the B1.2 composition. On the other hand, the L values of the developed bodies increased because of the low iron and titan content of the enriched kaolins.

Rapid firing behavior curves of standard and new developed compositions are given in Figure 4 which show the sintering rate with increasing temperature and shrinkage behavior of the body versus time. The temperature at which the sintering rate was the fastest in the standard body corresponds to 1210 °C, and this value was obtained as 1211 °C in both developed compositions.

Physical and Thermal Properties			STDB1	B1.1	B1.2
Kaolin 1		%	-	-	14
Kaolin 2			-	28	14
Ukrainian Kaolin			28	-	-
Clay			21	21	21
Feldspar			51	51	51
Max. Firing Temperature		^{0}C	1205	1205	1205
Firing Time		min.	61	61	61
Size		mm	46.48	45.72	46.02
Firing Shrinkage		%	7,50	9.01	8.42
Water Absorption		%	0,00	0,04	0.93
Color	L	-	81.55	83.16	82,67
	a	-	0.78	0.84	1.08
	b	-	9.38	8.63	7.97
Coefficient of Thermal Expansion	α_{300} °C x 10^{-7}	K^{-1}	63.48	62.33	65.65
	α_{400} °C x 10^{-7}		65.70	64.50	67.93
	α_{500} °C x 10^{-7}		68.92	66.77	70.33
	α_{600} °C x 10^{-7}		73.20	71.55	75.83

Table 3: *Physical and Thermal Properties of the Developed Body Compositions*

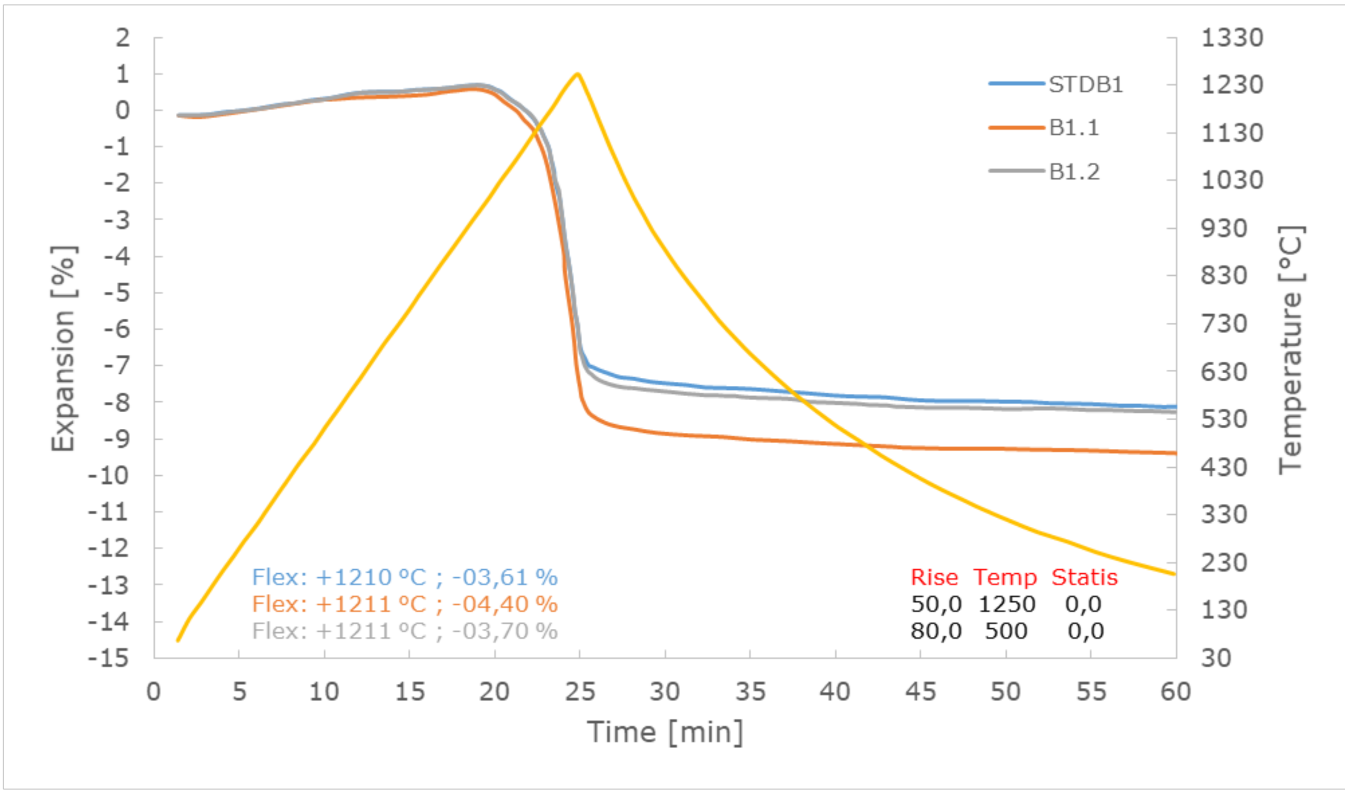


***Figure 4**: Rapid Firing Behavior Curves of the Standard and Developed Body Compositions.*

3) PHYSICAL AND THERMAL PROPERTIES OF THE DEVELOPED ENGOBES

Kaolin 1 and Kaolin 2 were used instead of the Ukrainian kaolin in certain percentages for porcelain engobe compositions (Table 4). No significant difference was observed in water absorption values, especially in compositions where Kaolin 2 was used in high ratios. The color values (L) of the developed engobes were very close to the color value (L) of the standard engobe. The thermal expansion coefficients of the developed compositions (E1.2, E1.3 and E1.4) were close to those of the standard composition, except for the E1.1 composition.

The sintering behavior of the engobes was studied with a non-contact optical dilatometer device (Figure 5). While the composition with the highest flex point (1029 °C) was E1.2, the compositions with the lowest flex point (this temperature was 953 °C in both compositions) were E1.1 and E1.4.

Physical and Thermal Properties			STDE1	E1.1	E1.2	E1.3	E1.4
Kaolin 1		%	-	4	-	-	-
Kaolin 2			-	-	4	6	12
Ukrainian Kaolin			12	8	8	6	-
Alumina			3	3	3	3	3
Clay			9	9	9	9	9
Quartz			30	30	30	30	30
Feldspar			12	12	12	12	12
Frit			27	27	27	27	27
Zirkon			7	7	7	7	7
Max. Firing Temperature		^{0}C	1205	1205	1205	1205	1205
Firing Time		min.	61	61	61	61	61
Water Absorption		%	0.04	0.04	0.09	0.04	0.00
Color	L	-	87.71	87.59	87.77	87.20	87.85
	a	-	-0.35	-0.29	-0.34	-0.29	-0.35
	b	-	1.30	1.22	1.32	1.13	1.37
Coefficient of Thermal Expansion	α_{300} °C x 10^{-7}	K^{-1}	62.26	65.07	65.13	66.29	62.06
	α_{400} °C x 10^{-7}		65.58	68.27	68.22	69.28	65.42
	α_{500} °C x 10^{-7}		69.39	72.10	71.91	73.01	67.57
	α_{600} °C x 10^{-7}		77.34	80.67	80.11	81.48	74.17

Table 4: *Physical and Thermal Properties of Developed Engobe Compositions*

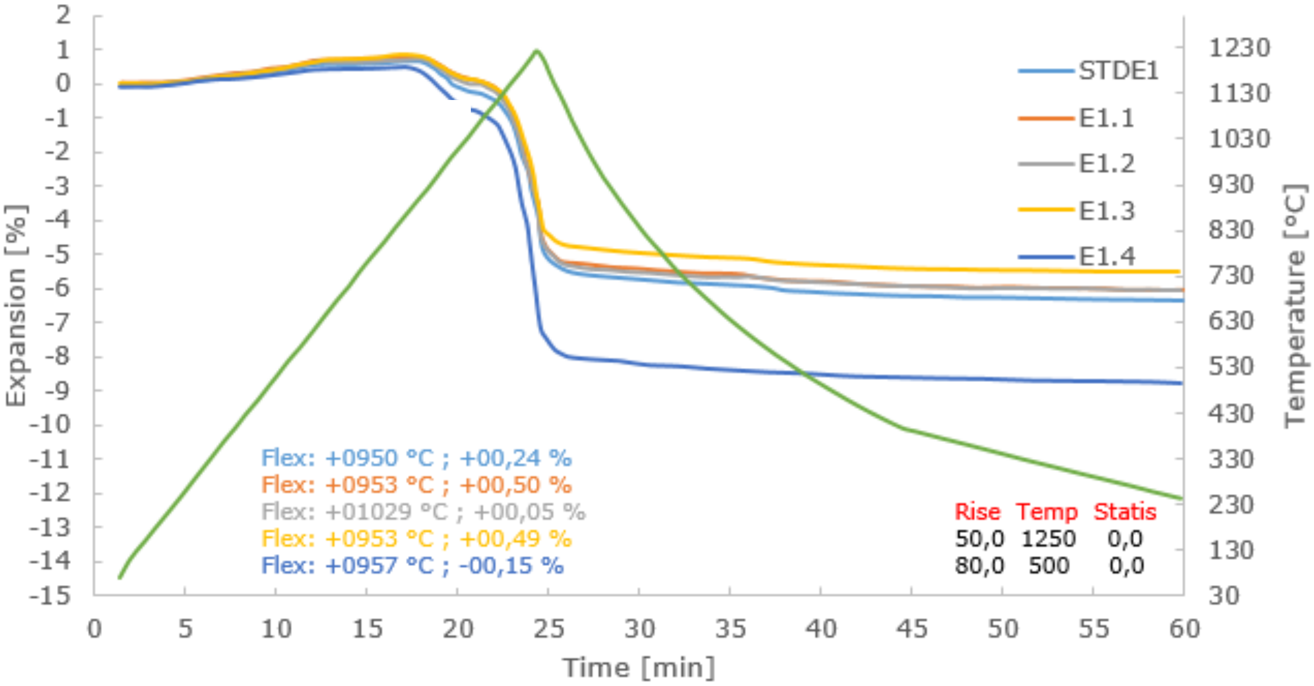
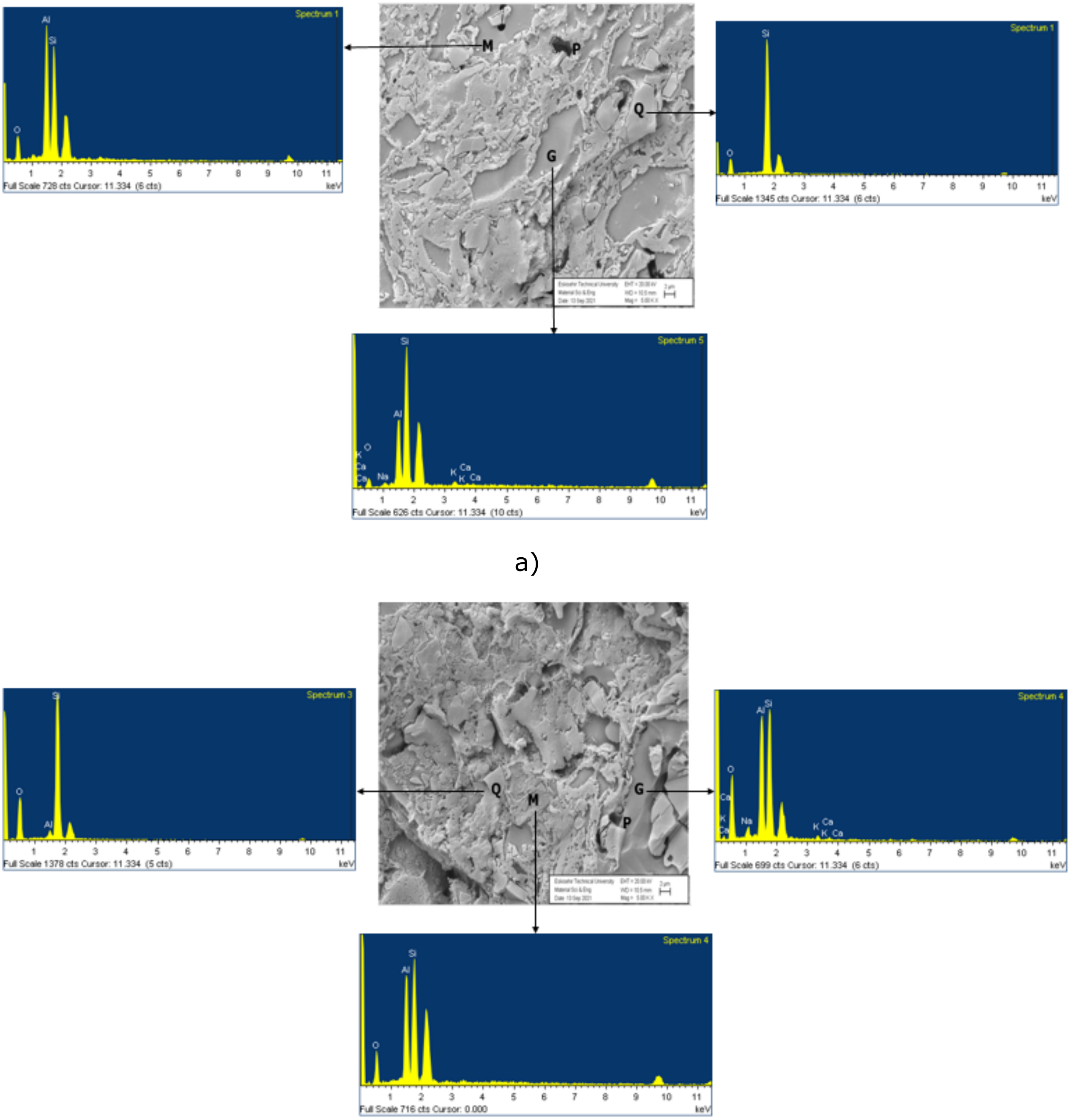


***Figure 5**: Rapid Firing Behavior Curves of the Standard and Developed Engobe Compositions.*

4) MICROSTRUCTURAL ANALYSIS OF THE PORCELAIN BODIES

Microstructures of the standard porcelain body (STDB1) and the developed body (B1.2) were examined by SEM (Figure 6). Mullite (M), quartz (Q) and glassy phases (G) were detected from the microstructure images. The presence of these crystalline and amorphous phases was supported by EDX.



a)

b)

***Figure 6**: SEM images of a) STDB1 and b) B1.2 porcelain bodies (M: mullite, Q: quartz, G: glassy phase and P: pore).*

CONCLUSION

In this study, the possible use of Western Anatolian kaolins containing high amounts of alunite in porcelain body and engobes was investigated by means of flotation as an enrichment method. The chemical, mineralogical, physical, and thermal properties of enriched kaolins and their use in porcelain bodies and engobes were examined. All these results indicate that lowering the SO_3 content of alunite-bearing kaolins will provide the necessary raw material supply for the ceramic industry, enabling the commercial use of such high content alunite present in kaolin deposits.

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