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PRE-CONCENTRATION AND FLOTATION OF ALUNITIC KAOLIN AND ITS POSSIBLE USE IN CERAMIC TILE INDUSTRY

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Abstract: The aim of this research was to remove sulphur and alunitic parts by the flotation method from alunitic kaolin obtained from the Balikesir-Sindirgi region of Turkey, which is not currently used by the ceramic industry because of its high sulphur content. In the process, mineral alunite was floated while kaolinite was depressed. The effect of pre-concentration on the flotation process was also investigated. Pre-concentration included several processes such as wetting, mechanical scrubbing, and screening for removal of fine alunite particles and colouring oxides from kaolin as well as screening after consecutive milling for the separation of hard minerals such as quartz from kaolin. After the pre-concentration and flotation processes, kaolin concentrate having a SO₃ content of 0.48% was obtained with a sulphur removal efficiency of 88.55%, and this kaolin was coded as F4. Afterwards, the use of F4 kaolin in the ceramic industry was investigated. For this purpose, the F4 kaolin was used in angobe preparation, and the angobes prepared were used for the production of floor and wall tiles. The properties of the angobes were also compared to those of commercial floor and wall tile angobes from a ceramic factory. These tests indicated that the floor and wall tile angobes prepared by using F4 kaolin could be used as an alternative for the angobes currently used by the factory.

Keywords: *alunitic kaolin, kaolin flotation, angobe, ceramic tiles*

Introduction

Kaolin has a wide range of industrial applications since it is a white coloured, fine grained, non-abrasive, and relatively cheap clay mineral with good coating and forming ability, low electrical conductivity, and easily dissolving nature in water (Bergaya et al., 2006; Murray, 2007; Castellano et al., 2010). Kaolin extracted from the commercial deposits contains kaolinite as a major component along with accessory minerals such as quartz, muscovite, limonite, anatase, hematite, illite, and organic matters. For industrial applications, kaolin must be extensively processed and highly

refined in order to be used as pigment, filler, coater, extender, and ceramic raw material. Coarser impurities (generally quartz) are easily separated by screening or classification while micrometer size impurities require special treatments. The partial or complete removal of these impurities by economical and practical methods has been the subject of many studies (Newns and Pascoe, 2002; Raghavan et al., 2004; Calderon et al., 2005; He et al., 2011).

Apart from the generally occurring impurities given above, there are more than 12 kaolin deposits in Turkey where sulphur is the major impurity. Sulphur in these deposits is generally associated with pyrite and/or alunite. The physical and chemical characteristics (except sulphur content) of the kaolin extracted from these deposits are generally suitable for ceramic production. Since sulphur causes cracks and pores during firing at elevated temperatures, it is impossible to use such ores in ceramic production directly. Therefore, SO_3 content of such raw materials must be reduced to lower than 0.5% (Ekmekci et al., 2001). Unfortunately, the sulphur content of the kaolin deposit within the Balikesir-Sindirgi region of Turkey is also very high hindering its use in the ceramic industry.

Typical methods used for the separation of alunite from kaolin are thermo-chemical, physico-chemical, and physical methods (Koca, 1992). From literature reviewed on the sulphur content of Balikesir kaolins at fractional base, it was realized that sulphur accumulated at finer fractions ($\sim 38 \mu\text{m}$). In other words, alunite particles existed together with mineral kaolinite (Girgin et al., 1993; Yapa, 1994). As seen from Table 1, it is rather difficult to remove alunite from kaolin at such fine fractions by using physical methods. The sulphur content of alunitic kaolins can be reduced by employing thermo-chemical methods (Table 2). In such methods, however, it is necessary to keep the roasting temperature of the thermal process well below the decomposition temperature of kaolinite to avoid any undesired physical and chemical changes in the properties. As explained from the related studies, the chemical structure of the kaolinite starts to change after 600°C , and it is converted to metakaolin (Ekmekci et al., 2001). With this change to metakaolin, kaolin loses its plastic property which is one of the most crucial parameters in ceramic production.

Table 1. Beneficiation of alunitic kaolin by physical methods

Reference	Process applied	SO_3 in the feed (%)	SO_3 in kaolin concentrate (%)	SO_3 removal efficiency (%)
Sumer, 1991	Comminution and classification	13.87	13.62	–
Acar, 1995	Mechanical scrubbing and classification	4.73	4.23	–
Ekmekci, 2001	Mechanical scrubbing and classification	1.09	Not beneficiated	–

Table 2. Beneficiation of alunitic kaolin by thermal methods

Reference	Roasting temperature (°C)	SO ₃ in the feed (%)	SO ₃ in kaolin concentrate (%)	SO ₃ removal efficiency (%)
Sumer, 1991	900	12.73	2.14	-
	1100	13.37	0.43	-
Girgin, 1993	600 (with 5% Na ₂ CO ₃ addition)	7.15	0.48	-
Genc, 1994	900	10.10	1-1.5	-
	700 (with KCl, NaCl addition)	10.10	1-3	(91.5-92.1)
Ekmekci, 2001	1000	1.09	0.48	-

Therefore, physico-chemical methods are regarded to be the most effective methods to reduce the sulphur content of alunitic kaolin to a desired level (<0.5%) for its use in the ceramic industry without altering its chemical and physical properties. From the very limited studies carried out to remove alunite from kaolin at fine particle sizes, it was observed that the efficiencies of such processes were rather low (Table 3). The reason for low efficiencies was explained by the fact that liberation could be obtained at particle sizes finer than 10 µm, which in turn, caused a slime coating problem during the process (Koca, 1992; Miller and Acherman, 1980).

Table 3. Beneficiation of alunitic kaolin by flotation

Reference	Flotation stage	SO ₃ in the feed (%)	SO ₃ in kaolin concentrate (%)	SO ₃ removal efficiency (%)
Sumer, 1991	One stage	10.07	8.36	-
Koca, 1992	One stage	17.85	Not beneficiated	-
Yapa, 1994	Two stages	1.94	0.22	39.60
Ekmekci, 2001	Two stages	1.09	1.06	18.24

In the ceramic industry, angobe production is one of the most common utilization areas for kaolins, if its physical and chemical properties are suitable. As is well known, red firing clays and some industrial waste materials are commonly used as starting materials in ceramic tile production whose final products are not white in colour. Therefore, angobe application is required in floor and wall tile production to improve aesthetic and/or functional properties before glazing. The use of frit glazing increases the cost of tile production; however, greyish appearances and dark shadows may occur when raw glazes are used. These types of glazing problems can also be solved by angobe application in ceramic tile production.

Angobe is a semi-liquid, viscous, and finely grained ceramic product which tends to give a dry-matt surface on its own and is generally used under a clear glaze. After

application, angobe slurry covers ceramic bodies at a desired density and colour, eliminates any thermal expansion disconformity between the glaze and the body and reduces the water absorption properties of the product. Moreover, production cost and glaze consumption is reduced; adhesion of fast firing glazes to the body can be maintained by angobe application (Ryan and Radford, 1987; Stefanov and Batschwarov, 1985).

In general, the floor and wall tile angobe compositions include such raw materials as clay, kaolin, quartz, feldspar, frit-type of semi-raw materials, oxides such as zirconium oxide, zinc oxide, aluminium oxide, and ceramic paints. The ratio of such ingredients in angobe composition may vary according to parameters such as body composition, firing temperature, firing duration, and glaze composition. However, a typical commercial floor and wall tile angobe recipe composition is comprised of 30-40% clay, 10-15% feldspar, 5-15% quartz, 5-10% zircon, and 10-20% frit. These ingredients are used in angobe recipes after removing the impurities and being comminuted to micron sizes (Kingery et al., 1973). Production stages of an angobe are summarized in Fig. 1.

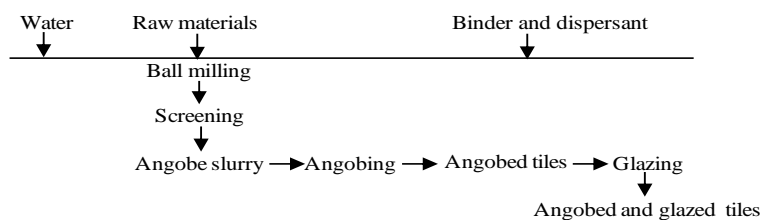


Fig. 1. Production stages for angobes

In this study, flotation method was employed to reduce sulphur content of alunitic kaolins obtained from the Balıkesir-Sındırgı region of Turkey, which is the largest kaolin deposit in the country, following mechanical scrubbing, classification, and grinding stages. Moreover, possible use of the kaolin concentrates whose sulphur content were reduced without heat treatment were investigated for angobe production which is a common practice in the ceramic tile industry.

Materials and methods

Materials

The alunitic kaolin used in the experiments was collected from the Balıkesir-Sındırgı region of Turkey, and the flotation method was applied to remove SO_3 from the kaolin. Preparation of the kaolins to be used in flotation tests were made by two different methods. In the first method, only the particle size of the kaolin was reduced, and then they were used in the flotation tests. The particle size of the kaolin was reduced to -2 mm by using jaw and roller type of crushers and then ground to -38 μm

using a ceramic ball mill of 2 L capacity. During grinding operations 3 different sized alubite balls were used as grinding media. Milling was carried out as wet at 50% solid concentration. In order to determine the optimum milling time, some milling tests were conducted at 60, 90, 120, 150, 180, 240 and 360 min. After milling, kaolin samples were dried and particle size analysis was made. After the tests, the optimum milling time for the kaolin was found to be 120 min. Consequently, raw kaolin samples were ground in the ball mill for 120 min and then passed through a 38 μm screen. The kaolin was then dewatered and dried at 100 °C before they were stockpiled for flotation tests. The kaolin samples prepared by this method were coded as NS.

In the second method, kaolin was subjected to mechanical scrubbing and screening operations (pre-concentration) and then used in the flotation tests. Before pre-concentration, the particle size of the kaolin was reduced to -2 mm using jaw and roller types of crushers. Afterwards, 500 g from this kaolin was taken to prepare a suspension at a solid/liquid ratio of 50% and then kept in water for 1 h. This was later mixed in a mechanical mixer at 1000 rpm for 30 min and screened through a 125 μm sieve. Under sieve was dewatered and dried then coded as S1. The over sieve was ground in a ball mill for 20 min and screened using a 125 μm sieve. The second under sieve was also dewatered and dried then coded as S2. The over sieve was ground in a ball mill for 20 min and screened using a 125 μm sieve again. The third under sieve was also dewatered and dried then coded as S3 (Fig. 2). The over sieve was removed as waste owing to the milling difficulties created by high quartz content. The S1, S2, and S3 kaolin samples obtained were used in the flotation tests.

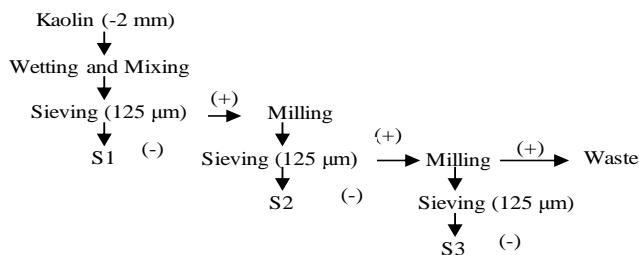


Fig. 2. Flow scheme for S1, S2 and S3 kaolin preparation

Chemical analysis of NS, S1, S2, and S3 kaolin samples was made using an XRF instrument (Rigaku-ZSX Primus II). Mineralogical analysis of the samples was made using an XRD instrument (Rigaku Miniflex ZD13113 series) using CuK α X-rays ($\lambda = 1.54056 \text{ \AA}$) in the range of 5-70° and at a rate of 2°/min. The variations in the colour of NS, S1, S2, and S3 kaolin samples were investigated using a Minolta colour measuring device. The micro structure of NS kaolin was investigated using a scanning electron microscope (ZEISS brand SUPRA 50 V model).

Methods

Preliminary tests were conducted to determine optimum flotation parameters such as the types and dosages of collector, frother and depressant, flotation time, pulp density, agitating rate, and pH. NS kaolin was used for these tests. The kaolin concentrates after these tests were coded as F1. S1, S2 and S3 kaolins were then floated at the optimum conditions, and the concentrates obtained were coded as F2, F3 and F4. DENVER type flotation cell of 1 L capacity was used for the flotation tests. In these tests, alunite was floated while kaolin was depressed using a depressant.

Angobe preparation

F4 kaolin whose SO_3 content was reduced after pre-concentration and flotation was used for angobe preparation. The properties of the angobes prepared by using F4 kaolin were compared to those of the angobes used by a ceramic factory in floor and wall tile production. The angobe recipes of the ceramic factory were taken as the reference and F4 kaolin was used in replace of quartz, kaolin, and aluminium oxides in the reference recipes. The composition of the angobe recipes prepared is summarized in Table 4, and the codes used in these tests were F, F1, W, and W1 for the reference floor tile angobe recipe, experimental floor tile angobe recipe, reference wall tile angobe recipe, and experimental wall tile angobe recipe, respectively.

Table 4. Floor and wall tile angobe compositions

Raw materials	Amount (%)			
	F	F1	W	W1
Kaolin	23.0	–	12.0	–
Quartz	12.0	–	21.0	5.8
Al_2O_3	4.0	0.8	–	–
Others	61.0	61.0	67.0	67.0
F4	–	38.2	–	27.2

The raw materials used for the preparation of the angobes were first weighed according to the ratios given in Table 4, and then ground in a jet mill for 32 min. The milling process was carried out as wet at a solid ratio of 72%. The material was then passed through a 100 μm sieve before being applied onto the surface of wall (WM) and floor (FM) tiles of the factory by pouring method. The amount of angobe for each tile was determined as 20 g. The angobed tiles were dried at 105 °C for 2 h. The dried tiles were fired at 1195 °C for 33 min (floor tiles) and 1130 °C for 33 min (wall tiles) in a roller type of industrial kiln of the factory. The reference angobed floor tile was coded as FA, the experimental angobed floor tile was coded as FA1, reference angobed wall tile was coded as WA, and the experimental angobed wall tile was coded as WA1.

An industrial glazing process was also applied to the angobed wall and floor tiles produced. The firing process of the angobed+glazed tiles was kept similar to that of angobed tiles. The material used in glazing was similar to those normally used for the glazing of floor and wall tiles in the factory. The reference angobed+glazed floor tile was coded as FG, the experimental angobed+glazed floor tile was coded as FG1, reference angobed+glazed wall tile was coded as WA, and finally experimental angobed+glazed wall tile was coded as WG1.

In order to find out whether the expansion characteristics of the floor and wall tile angobes prepared would be suitable when applied to the floor and wall tiles bodies of the factory, the thermal expansion coefficients of the angobes and the bodies were also determined. Moreover, the thermal expansion coefficients of the glazes used were determined to find out the suitability to the angobes and the bodies. Thermal expansion analysis of the angobes, bodies, and glazes were made using a dilatometer (NETZSCH DIL 402 PC).

In order to determine the colour differences between the surfaces of angobed and angobed+glazed tiles, colour measurements were made using a Minolta brand colour measuring device. The micro-structure of the angobed and angobed+glazed surfaces was analysed using a JEOL JSM-5600 V brand scanning electron microscope (SEM).

Finally, permeability and Harcourt tests were conducted on the angobed+glazed tiles. While the factory's standard method was used for the permeability tests, the Turkish National Standard procedure, coded as TS EN ISO 10545-9 (1997), was used as a method of determining thermal shock resistance of the tiles (Harcourt tests).

Results and discussions

Chemical analysis of kaolin

Chemical analysis of NS and pre-concentrated S1, S2, S3 kaolin is given in Table 5. As seen from Table 5, the amount of SiO₂ increases from S1 to S3. In other words, some of the quartz within the ore was removed from the over sieve at each stage of sieving after the mechanical scrubbing operation (Fig. 2). This result was caused by the low grindability of the free quartz within the kaolin composition. As shown in Table 5, the amounts of SO₃ and K₂O coming from alunite and other oxides were reduced from S1 to S3. This result can be explained by the fact that most of the fine

Table 5. Chemical composition of the kaolins (w/w %)

Samples	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	SO ₃	K ₂ O	L.O.I.
NS	55.24	25.58	1.08	0.38	4.05	1.08	11.88
S1	43.44	31.37	2.58	0.52	6.08	1.72	16.50
S2	56.19	25.87	0.65	0.35	4.34	1.10	12.21
S3	59.73	23.00	0.38	0.33	2.44	0.86	8.37

grained kaolinite, alunite minerals, and the colouring oxides within the ore are obtained from the under sieve. This result was also supported by the semi-quantitative chemical analysis given in Table 6.

Table 6. Semi quantitative analysis of NS, S1, S2, S3 kaolins

Samples	Kaolinite	Alunite	Quartz
NS	54.93	10.49	29.70
S1	64.66	15.75	13.37
S2	54.96	11.24	30.61
S3	52.31	6.32	35.39

Mineralogy of kaolin samples

Mineralogical analysis of the kaolin samples (NS, S1, S2 and S3) is given in Fig. 3. When the XRD pattern of NS kaolin is examined (Fig. 3), it is seen that SO_3 and K_2O in the chemical composition originated from alunite mineral ($\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$). Alunite peak in S3 kaolin is much lower than those of NS, S1 and S2. This result proved that alunite was removed from the NS body by mechanical scrubbing-milling-sieving operations.

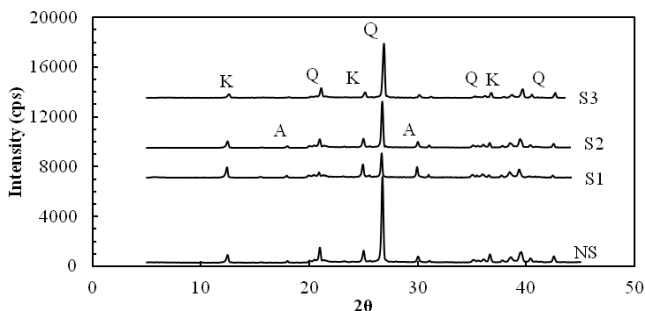


Fig. 3. XRD patterns of NS, S1, S2, S3 kaolins (K: kaolinite, A: alunite, Q: quartz)

Colour measurements of kaolin samples

Colour values (Lab) of the kaolin samples (NS, S1, S2 and S3) are presented in Table 7. As seen from Table 7, whiteness of the kaolin samples (L value) was increased from S1 to S3. This indicated that most of the colouring oxides (TiO_2 and Fe_2O_3) were

Table 7. Colour values of NS, S1, S2 and S3 kaolins

Samples	L	a	b
NS	74.87	9.23	19.15
S1	72.35	8.22	18.70
S2	82.74	4.92	11.13
S3	91.09	2.40	3.55

removed at each stage of milling and sieving during pre-concentration. This result was also supported by the decrease in positive “a” and “b” values (meaning a decrease in yellowish-reddish colours) from S1 to S3. This result is also in good correlation with the results given in Tables 5 and 6.

Lab colour plane (Fig. 4) was used for the interpretation of the colour values. L is a scale for brightness/darkness and it ranges from “100” for a perfect white to “0” for an absolute black. Red/green is designated by “a” and higher positive values of “a” denotes more red colouring. The higher negative value of “a”, means that there is greener colour in the environment. Yellow/blue is designated by “b”, positive values of “b” refer yellowish colour whereas negative “b” values define bluishness (Chandrasekhar and Ramaswamy, 2006).

Additionally, the micro structure of NS kaolin is given in Fig. 5. Rhombusal alunite minerals (5-10 μm in particle size) are seen in kaolinite and quartz minerals (Fig. 5).

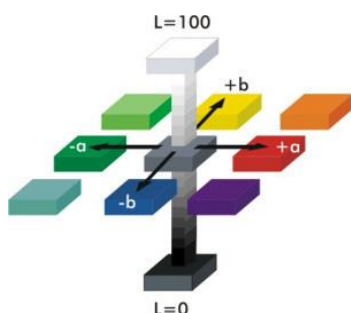


Fig. 4. CIE Lab colour plane (Ozcan, 2008)

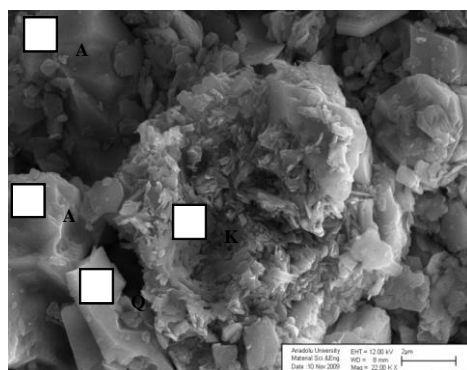


Fig. 5. SEM picture of the NS kaolin (K: kaolinite; A: alunite; Q: quartz)

Results

Flotation tests

The parameters used to determine optimum conditions for NS kaolin flotation are summarized in Table 8. The first experiment was carried out to determine the type and amount of collector and successive tests were performed using the previous optimum result.

Effect of dosage and type of collector

Four different types of anionic collectors were tested in order to determine the suitable collector type for the flotation of alunite which was sodium oleate, AERO 825, AERO 801 and AERO 845. The dose of 3000 g/Mg for each collector type were used in the

Table 8. Flotation test parameters

Parameters	Values	Parameters	Values
Particle size	-38 μm	Flotation time	1-6 min
Type of collector	Na Oleate, AERO-825, 801, 845	Conditioning time (for depressant)	1 min
Collector dosage	0.5-3.5 kg/Mg	Conditioning time (for collector)	5 min
Type of frother	MIBC, pine oil	Pulp density (solid rate)	5%-15%
Frother dosage	0-120 g/Mg	Agitation rate	900-1400 rpm
Type of depressant	Sodium silicate	pH	4.5-9.5
Depressant dosage	0-700 g/Mg		

experiments and SO_3 grades in kaolin concentrates were measured. SO_3 grades were measured as 2.94%, 2.47%, 2.97%, and 2.10% when sodium oleate, AERO 825, AERO 801 and AERO 845 were used, respectively. Since the lowest SO_3 grade was obtained with AERO 845, it was chosen as the optimum collector type for NS kaolin flotation.

For the determination of optimum dosage, the flotation tests were carried out using 500, 1000, 1500, 2000, 2500, 3000, and 3500 g/Mg of AERO 845. The obtained SO_3 grades in the kaolin concentrates and the sulphur removal efficiencies were summarized in Fig. 6a. As the collector dosage increased, the sulphur removal efficiencies increased while the SO_3 grades in the kaolin concentrates were reduced up to a point (Fig. 6a). When the collector dosage exceeded 3000 g/Mg, the effect of collector quantity to the efficiency was reversed. In flotation, if an excessive amount of collector is used, particle surfaces may be covered by collectors as a multi-layer rather than a mono-layer. This phenomenon may reduce the hydrophobicity of the particles since the non-polar parts of the collector molecule cannot orient into the solution. Moreover, excessive collector usage increases the possibility of bubble collision in the froth and may cause the particles attached to the air bubbles to return to the pulp. Therefore, collectors must be used at optimum quantity and it is typically considered that excessive use of collectors reduces the efficiency of the flotation (Saklara et al., 1998).

As seen from Fig. 6a, the increase of SO_3 grades in the kaolin when more than 3000 g/Mg of collector was used was thought to be caused by the return of particles attached to the air bubbles to the pulp. As a matter of fact the size of the air bubbles was noticed to be considerably enlarged when more than 3000 g/Mg of collector was used. After the weighing of the concentrates and wastes of each experiments, it was also realized that this opinion was supported by the increase in the amount of kaolin (sunken part) when more than 3000 g/Mg of collector was used (Tatar, 2012). Therefore, 3 kg/Mg of collector was chosen as the optimum value since it provided the minimum sulphur grade in the kaolin concentrate and the highest sulphur removal

efficiency. At first glance, the amount of collector chosen can be considered to be rather high, however, this result was inevitable considering the very high specific surface area of the fine grained materials used (Mathur, 2002; Cilek, 2006).

Effect of dosage and type of frother

In order to determine the optimum frothing agent, the most common types of frothers such as pine oil and MIBC (methyl isobutyl carbinol) were used for the experiments. These frothers were used as 60 g/ton and the SO₃ grades in the kaolin concentrates were measured. After these tests, the SO₃ grades in the kaolin concentrates were determined as 2.77% and 1.77% when pine oil and MIBC were used, respectively. The bubbles were noticed to be fewer, smaller, and easily broken down when pine oil was used whereas the bubbles were larger and more durable when MIBC was chosen. Therefore, MIBC was selected as the frother owing to its better froth formation and the lower SO₃ grades in the kaolin concentrates obtained.

The flotation experiments were carried out using 0, 20, 40, 60, 80, 100, and 120 g/Mg of MIBC in order to find out the optimum dosage of the frothing agent. The obtained SO₃ grades in the kaolin concentrates and the sulphur removal efficiencies were summarized in Fig. 6b. As seen from Fig. 6b, the SO₃ grades in the kaolin concentrates were reduced as the frother dosage increased, that is to say, more alunite mineral were removed together with the froth occurred. This result is in good correlation with the literature. As a matter of fact, frothing agents create a homogeneous bubble size distribution and durable froth layer in a flotation system. These functions work better and a more durable and homogeneous froth occurs with the increase in the amount of frothing agent up to an optimum point. Hence, particle transfer from the pulp to froth phase becomes easier and the possibility of particle returning from the froth phase to the pulp decreases. In lower frother usage, the froth layer is easily broken down, obtaining mineral particles from the froth becomes more difficult and particles may tend to return to the pulp (Saklara et al., 1998). The grade and efficiency values did not change considerably when the amount of frothing agent used was more than 100 g/Mg. Therefore, it was selected as the optimum amount of frothing agent since it produced the lowest sulphur grade and the highest sulphur removal efficiency.

Effect of dosage and type of depressant

Sodium silicate is known as a good dispersant together with its depressant effect. It increases surface charge between the particles in the solution. Hence, the fine grained slam layer is easily dispersed and a clear mineral surface to react with collector is obtained (Wills and Napier, 2006). For these reasons, sodium silicate was chosen as a depressant in the tests. In order to find out the optimum depressant dosage, the experiments were carried out using 0, 100, 300, 500, and 700 g/Mg of sodium silicate. After the tests, the obtained SO₃ grades in the kaolin concentrates and the sulphur removal efficiencies were summarized in Fig. 6c. As seen from Fig. 6c, the SO₃ grades in the kaolin concentrates were decreased as the depressant dosage increased

up to 300 g/Mg. The effect was, however, reversed as the depressant dosage increased to more than 300 g/Mg. This can be explained by the fact that mineral particles to be floated are depressed as the amount of depressant used is increased above an optimum value. This result was proven in the tests in which more than 300 g/Mg of depressant were used by the increase in the weight of sunken part (kaolin) and by the decrease in the weight of floated part (alunite) (Tatar, 2012). As a result, 300 g/Mg was selected as the optimum depressant dosage to be used since it provided the minimum SO₃ grade in the kaolin concentrate and the highest sulphur removal efficiency in the waste.

Effect of flotation time

In order to determine optimum flotation time, several flotation tests were carried out for 1, 2, 3, 4, 5, and 6 min. The SO₃ grades in the kaolin concentrates were reduced as the flotation time was increased which is expected in a flotation process. Therefore, 5 min was chosen as the optimum flotation time since no further improvement was obtained at longer periods.

Effect of pulp density

Various pulp densities such as 5%, 10% and 15% were prepared to determine the optimum value. After the tests, the obtained SO₃ grades in the kaolin concentrates and the sulphur removal efficiencies were summarized in Fig. 6d. As seen from Fig. 6d, SO₃ grades in the kaolin concentrates were only slightly increased as the pulp density was increased. This result can be considered to be normal since the distribution of the air flow in the cell owing to the changes in the pulp density is changed and free bubble surfaces are decreased. Therefore in general, efficiency of the separation decreases with the increase in the pulp density (Saklara et al., 1998).

Consequently, 5% was chosen as the optimum pulp density for the flotation tests since the SO₃ grade in the kaolin concentrate was the minimum although there was no noticeable change in the sulphur removal efficiency. A pulp density of 5% should not be considered as too low in a flotation process of finely grained minerals (Mathur, 2002).

Effect of agitation rate

To determine the optimum agitation rate for the flotation tests, 900, 1000, 1100, 1200, 1300, and 1400 rpm were tested. After the tests on the prepared pulps, the obtained SO₃ grades in the kaolin concentrates and the sulphur removal efficiencies were summarized in Fig. 6e. As seen from Fig. 6e, the SO₃ grades in the kaolin concentrates were decreased as the agitation rate increased up to 1200 rpm. This result is considered to be normal since increasing the agitation rate up to an optimum point increases the efficiency of the separation by increasing particle-bubble contact and the probability of collision within the flotation cell. Increasing the agitation rate also promotes the dispersing effects onto the fine grains. Hence, interaction between the

clean particle surfaces and the chemical reagents is increased and removal of the particles by air bubbles can be performed easily (Cilek, 2006).

Again from Fig. 6f, the SO₃ grades in the kaolin concentrates were seen to be increased after agitation rates of over 1200 rpm. This was thought to have occurred by the break off the aggregates (particles attaching the air bubbles) from the bubbles as a result of turbulence caused by the high agitation rates. Consequently, 1200 rpm was selected as the optimum agitation rate since the SO₃ grade in the kaolin concentrate was the minimum and the sulphur removal efficiency was the maximum.

Effect of pH

The tests were carried out in order to determine the optimum pH values for the flotation tests using pulp pH values of 4.5, 5.5, 6.5, 7.5, 8.5 and 9.5. After the tests with these pH values, the obtained SO₃ grades in the kaolin concentrates and the sulphur removal efficiencies were summarized in Fig. 6f which reveals that the SO₃ grades in the kaolin concentrates increased together with the increase in pH values.

As is well known, mineral behaviours such as dispersion, aggregation and flotation depend on surface charges. From the studies in which the surface charges of the minerals (kaolinite, alunite and quartz) within the kaolin ore used with respect to pH were investigated and it was found that the zero point of charge (zpc) for alunite were determined at pH 7.2 (Koca, 1992; Dixit, 1980) and pH 10.3 (Kosmulski, 2009). However, Ustaer (1975) could not determine the zpc value for alunite in his research. According to Ustaer's findings, the surface charge of alunite remains positive at all pH values. On the other hand, the zpc for kaolinite were mostly determined at between pH 2 and pH 4.5 (Kosmulski, 2009; Dikmen et al., 2011). From the findings of these studies, it was understood that the zpc for kaolinite became negative after these pH values. Quartz was also reported to have similar surface charges with kaolinite (Kosmulski, 2009). As a summary, while there was not much difference in the zpc values of quartz and kaolinite, it was found to be considerably diverse for alunite which was thought to be caused by the differences in their origins. Moreover, the adsorption of anionic collectors onto the alunite surfaces was negatively increased depending on the collector concentration and pH (Koca 1992). As a matter of fact, the highest alunite flotation recovery was obtained at slightly acidic-alkali pH values (pH 5-9) from the pH based flotation experiments (Miller and Misra, 1985; Miller and Acherman, 1980; Dixit 1980).

In this research, sulphur removal efficiencies obtained according to pH variation did not exhibit considerable differences and reasonably high efficiency values were achieved (Fig. 6f). The SO₃ grades within the kaolin were slightly increased. The reason for that can be explained by the fact that alunite approached its zero point of charge and hence the adsorption of anionic reactive (AERO 845) was decreased on the surfaces of alunite. Therefore, it was decided to use pH 8.5 (natural pH value) as the optimum pH value in the flotation tests. Consequently, the corrosion within the

flotation cell and the pipes was kept to a minimum and acid use was not needed to arrange pH, by choosing an alkali media at pH 8.5 (Pearse, 2005).

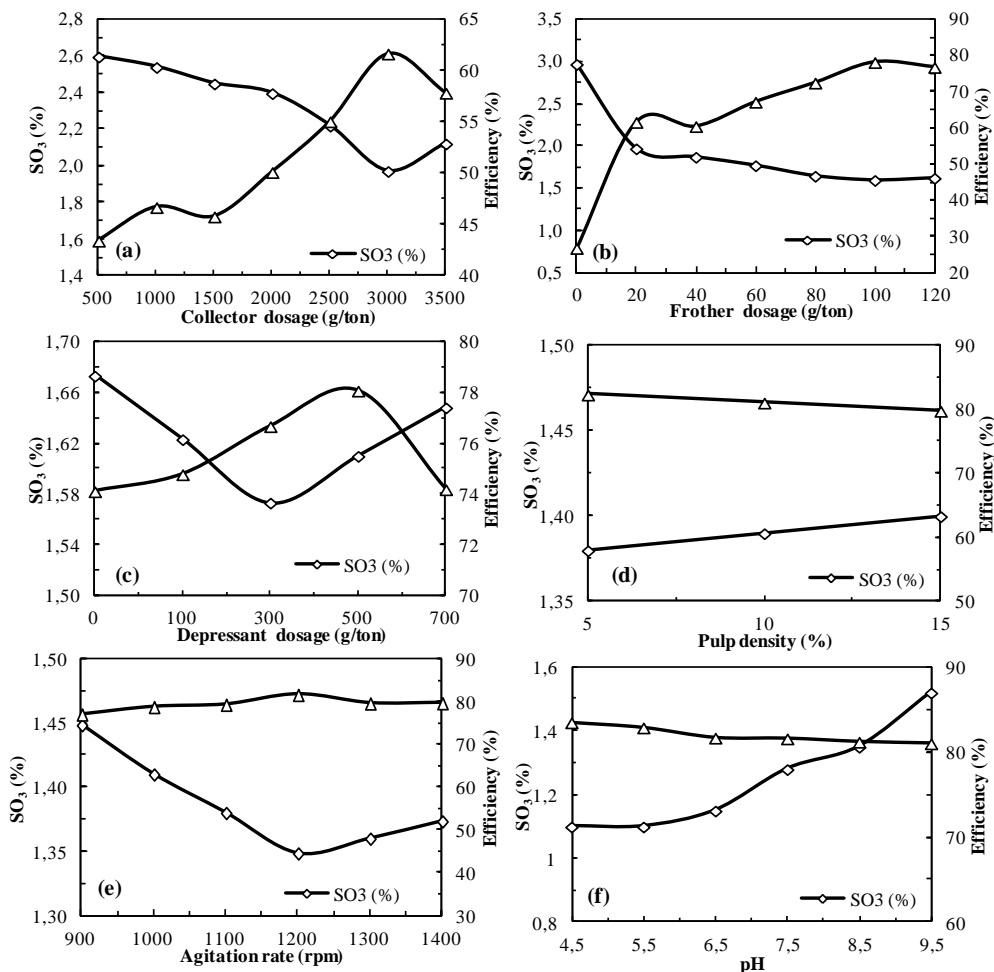


Fig. 6. Effect of (a) collector dosage (b) frother dosage (c) depressant dosage (d) pulp density (e) agitation rate (f) pH on flotation

Summary of the flotation test results

The optimum parameters selected for the flotation of alunitic kaolin (NS) are given in Table 9. In order to determine the effect of pre-concentration to the flotation of alunitic kaolin (NS), flotation tests were applied to the pre-concentrated kaolins (S1, S2, S3) under the same conditions. The obtained SO₃ grades in the kaolin concentrates and the sulphur removal efficiencies are summarized in Table 10.

Table 9. Optimum flotation parameters for NS kaolin

Parameters	Values
Collector dosage	3000 g/Mg AERO 845
Frother dosage	100 g/Mg MIBC
Depressant dosage	300 g/Mg sodium silicate
Flotation time	5 min
Pulp density	5%
Agitation rate	1200 rpm
pH	8.5

Table 10. Flotation test results for NS, S1, S2, S3 kaolins

Kaolin samples	SO ₃ in the feed	SO ₃ in the kaolin concentrate	SO ₃ removal efficiency
	(%)	(%)	(%)
NS	4.05	1.35 (F1)	81.22
S1	6.08	2.33 (F2)	79.09
S2	4.34	1.33 (F3)	80.28
S3	2.44	0.48 (F4)	88.55

As seen from Table 10, the SO₃ grade in the concentrate of S3 kaolin after flotation was found to be as low as 0.48%. Since this kaolin concentrate (F4) could be used in ceramic industry, the following tests were done to prove its use in wall and floor tile angobe production.

Angobe production

Thermal expansion

One of the most important task of the angobes is to eliminate the thermal expansion disconformity between the glaze and the body. Otherwise, flaws grow within the glaze and chipping could occur. Thermal coefficients of the angobes prepared by F4 kaolin (F1, W1), tile bodies of the factory (FM, WM), the angobes of the factory (F, W), and the glazes of the factory (GF, GW) at 400 °C were measured. The results are given in Table 11.

Table 11. Thermal expansion coefficient of the angobes, bodies and the glazes

Thermal expansion coefficient ($\alpha(1/K).10^{-6}$)	FM	F	F1	GF	WM	W	W1	GW
	6.80	5.64	6.30	6.40	6.90	6.92	7.16	5.90

As a general rule, thermal expansion coefficient of a glaze must be concordant to that of a body. As seen from Table 11, the thermal expansion coefficient of the floor tile angobe of the factory (F) was much lower than that of the body (FM). On the other hand, the thermal expansion coefficient of the floor tile angobe (F1) prepared by using F4 kaolin was higher than that of the angobe called F. Therefore, thermal expansions

of the angobe, glaze, and the body will be in more harmony if F1 angobe is used. Again it is seen from Table 11 that the thermal expansion coefficient of the wall tile angobe (W) of the factory is almost similar to that of the body (WM). The thermal expansion coefficient of the wall tile angobe (W1) prepared by using F4 kaolin is slightly higher than that of the W angobe. In order to find out the conformity between the body, glaze and the angobe, Harcourt and Autoclave tests were carried out on the angobed+glazed wall tiles. The Harcourt and Autoclave tests were applied to both floor and wall tiles, and there were no chipping observed on the surface of the tiles tested. Permeability tests were also conducted on these tiles, and they proved to be impervious to water. In other words, the tiles tested did not emit the water absorbed by the body to the surface. This ensures that the decorative finish will remain stable during the use of the tiles.

Colour

Another important feature of angobes is to cover the surface colour and roughness at the desired colour and density. Generally, the surfaces of the wall and floor tiles are desired to be as white as possible. Therefore, L values of the angobed and angobed+glazed tiles were measured in order to determine the effect of the angobes prepared by F4 kaolin onto the surface whiteness of the bodies. The results are summarized in Table 12.

Table 12. Whiteness of the angobed and angobed+glazed wall and floor tile surfaces

L	FA	FA1	FG	FG1	WA	WA1	WG	WG1
Value	82.94	82.01	86.54	87.97	91.75	91.25	90.10	89.71

As seen from Table 12, the whiteness value of the FA1 surface is slightly lower than that of the FA surface. It means that the coating ability of the F1 angobe is slightly lower than that of the F angobe. This situation can easily be seen from Figs. 7 (a) and (b) where the FA1 surface has a more porous texture than the FA surface. On the other hand, the whiteness value of the FG1 surface is higher than those of both FA and FG which indicates that the coating ability of the F1 angobe increased after glazing. This is corrected by the similar SEM pictures of FG and FG1 surfaces given in Figs. 7 (c) and (d). Consequently, it is clearly seen from these results that the F1 angobe could be used as an alternative for the F angobe of the factory for floor tiles.

For wall tiles, the whiteness of the WA1 surface is almost similar to that of the WA surface (Table 12). The micro-structure of the tiles in Figs. 8 (a) and (b) are seem to be similar as well. Similarly, the micro-structure and the whiteness of the glazed surface of these tiles (WG and WG1) are quite identical as seen in Figs. 8 (c) and (d). Therefore, the W1 wall tile angobe can easily be used as an alternative for the W angobe of the factory.

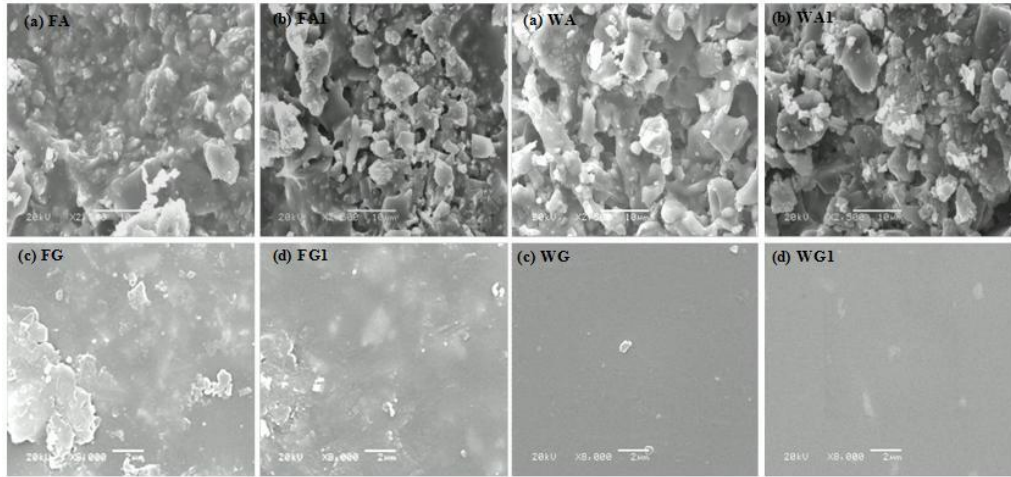


Fig. 7. SEM pictures for the angobed and the angobed+glazed floor tiles

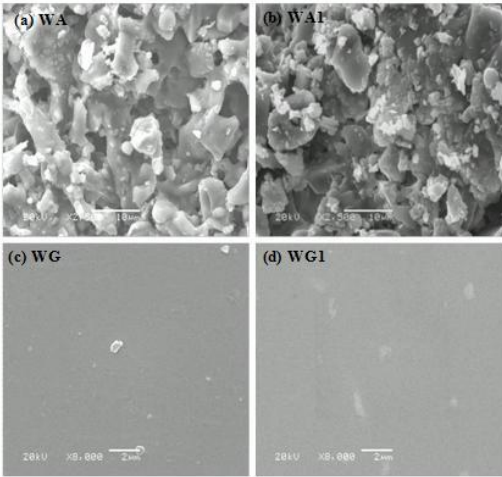


Fig. 8. SEM pictures for the angobed and the angobed+glazed wall tiles

Conclusions

In this research, the prepared floor tile angobe (F1) and wall tile angobe (W1) were used as alternatives for floor and wall tile angobes of a ceramic factory, respectively. These angobes were prepared by using F4 kaolin which was obtained by the flotation of pre-concentrated kaolin samples. The main results of the research are as follows.

- It was found that the Balıkesir-Sındırgı kaolins contained 4.05% SO_3 within the composition and were comprised of mineral kaolinite, alunite, and quartz.
- Most of the alunite and colouring impurities within the composition of the Balıkesir-Sındırgı kaolins were removed by using pre-concentration techniques such as wetting and mechanical scrubbing. After the pre-concentration process, the whiteness of the kaolin was considerably increased.
- After flotation of kaolin with 4.05% SO_3 content, the kaolin concentrate (F1) was obtained with a SO_3 grade of 1.35% and a sulphur removal efficiency of 81.22%.
- The kaolin concentrate (F4) was obtained with a SO_3 grade of 0.48% and a sulphur removal efficiency of 88.55% from the tests carried out to determine the effect of pre-concentration onto the flotation of Balıkesir-Sındırgı kaolin.
- From the tests conducted to determine possible use of F4 kaolin concentrate in ceramic industry, it was understood that the floor and wall tile angobes prepared by F4 kaolin could be used as alternatives for floor and wall tile angobes of a ceramic factory.
- Finally, the SO_3 content of the Balıkesir-Sındırgı kaolins were reduced to an acceptable level ($<0.5\%$) without using heat treatment which was the main obstacle for them to use in ceramic industry. This will make this material

extremely attractive for ceramic factories using angobes in their floor and wall tile productions.

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