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Desulphurisation Of İvrindi Alunitic Kaolin

İvrindi Alunitli Kaolininden Kükürdün Uzaklaştırılması

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ABSTRACT

In this paper, the results of degritting, classification, flotation, leaching and roasting tests carried out to produce a final product with acceptable sulphur content (<0.5 % SO_3) from İvrindi (Balıkesir-Turkey) alunitic kaolin are presented. Separation of alunite from kaolinite by physical separation methods was proved quite difficult, since alunite grains were also disintegrated to ultrafine particle size range as kaolinite. Both acidic and alkaline leaching tests were applied to reduce the sulphur content of the sample and a final product containing 0.73 % SO_3 was obtained by alkaline leaching. Although it was possible to obtain a final product with 0.48 % SO_3 by roasting at 1000 °C, due to conversion of kaolinite into metakaolinite, the casting property of the sample affected adversely.

Key words: Alunitic kaolin, classification, desulphurisation, flotation, leaching, roasting.

ÖZ

Bu yazıda, İvrindi (Balıkesir-Türkiye) alunitli kaolininden kabul edilebilir kükürt içeriğine (<% 0.5 SO_3) sahip bir son ürün elde etmek amacıyla yapılan kil açma, sınıflandırma, flotasyon, liç ve kavurma deney sonuçları verilmiştir. İvrindi kaolin yatağında bulunan alunit tanelerinin açma işlemi sonrasında, kaolinit taneleri gibi çok ince tane boylarında olması nedeniyle, fiziksel yöntemler kullanılarak alunit tanelerinin kaolinden ayrılmasının zor olduğu belirlenmiştir. Örneğin kükürt içeriğinin azaltılması amacıyla hem asidik, hem de alkali liç yöntemleri uygulanmış, ancak alkali liç sonrasında sadece % 0.73 SO_3 içeriğine sahip bir son ürün elde edilebilmiştir. Kavurma deneylerinde 1000 °C sıcaklıkta % 0.48 SO_3 içerikli bir son ürünün elde edilmesine karşın, döküm özelliklerini olumsuz yönde etkileyen meta-kaolinit fazının oluşması bu sıcaklıkta gerçekleşmiştir.

***Anahtar kelimeler**: Alunitli kaolin, sınıflandırma, kükürdün uzaklaştırılması, flotasyon, liç, kavurma*

INTRODUCTION

Kaolin is one of the most valuable industrial clays whose commercial value is determined by its whiteness, chemical purity, particle size distribution, etc. The kaolin extracted from the commercial deposits contains kaolinite as the major component together with accessory minerals, such as quartz, muscovite, limonite, anatase, hematite, illite and organic matter. For industrial applications, kaolin must be extensively processed and refined in order to be used as pigment, filler, coater, extender and ceramic raw material, etc. The partial or complete removal of these impurities in an economical manner has been the subject of many researches. The coarser impurities, generally quartz, are quite easily separated by screening or classification, while the micron size impurities require special vigorous treatment.

Apart from the generally occurring impurities given above, there are more than 12 kaolin deposits in Turkey where sulphur is the major impurity (Alpar et al., 1973). The 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 %.

Sulphur content of alunitic kaolin is generally reduced by thermo-chemical method in which the raw material is subjected to temperatures of 900 °C or higher (Can and İndel,1988). The required roasting temperature can also be reduced to 600 °C by addition of 2-5 % of Na_2CO_3 or NaCl during roasting and leaching of the roasted material by water (Girgin et al., 1993). There are also a few publications dealing with separation of alunite from kaolinite by selective flocculation and flotation (Koca and Özdağ, 1994; Abdel-Khalek et al., 1996; Gebhardt, et al., 1998). However, these studies are in laboratory scale and do not have any possibility for industrial application due to the difficulties encountered mainly from ultrafine particle size of clays.

In this study, following degritting and classification stages, flotation, leaching and roasting tests were applied to decrease the sulphur content of alunitic kaolin sample taken from İvrindi- Balikesir (Turkey) and to produce a final product suitable for ceramic production.

MATERIAL AND METHODS

Ore Characterization

Alunitic kaolin sample was obtained from İvrindi (Balikesir) district in the western part of Turkey. Table 1 shows the main chemical composition of the sample. As it can be seen from Table 1, the sulphur and iron contents of the sample are beyond the acceptable limits for ceramic production.

Mineralogical studies indicated that the major constituent was kaolinite. Quartz was the abundant impurity. Alunite $[KAl_3(SO_4)_2(OH)_6]$, being the source of sulphur in the sample, was detected by XRD (Figure 1). The iron contaminants were identified mostly as staining on the kaolinite grains, but free geothite grains were also recorded.

Methods

Degritting and classification tests

The sample was crushed to -10 mm with a jaw crusher and divided into representative samples of approximately 2 kg. lots. Degritting tests were carried out in a scrubber at a pulp density of 50 % solid by weight and impeller speed of 1500 rpm for 10 minutes. The pulp was then sieved through 300 μm and a 50 mm Mozley hydrocyclone with 6.4 mm vortex and 14.3 mm apex diameters was used for classification. The oversize of the sieve was regarded as grit.

Table 1. Chemical composition of İvrindi alunitic kaolin sample

Çizelge 1. İvrindi alunitli kaolin numunesinin kimyasal bileşimi

Component	%
Al_2O_3	31.26
SiO_2	52.41
CaO	1.13
Fe_2O_3	2.77
SO_3	1.10
K_2O	0.17
Na_2O	0.06
TiO_2	0.76
LOI	10.34

Flotation test

The flotation conditions applied in the flotation of İvrindi alunitic kaolin was chosen based on the flotation test results in the literature (Gebhadrt et al., 1998). After degritting, the –38 μm material obtained by wet sieving was used for the flotation tests. AERO Promoter 845 and Na-Oleate were employed as promoter and collector respectively. Sodium silicate was used as a dispersant. The pH was adjusted to 6.5 using either NaOH or HCl. The flotation test was performed on a 15 % pulp density in a 1 lt. Denver cell. After pH adjustment, sodium silicate was added at dosage of 4 kg/t and conditioned for 5 minutes. The pulp was re-conditioned for 10 minutes with the collector and the promoter dosages of 1.7 and 0.8 g/t respectively. The flotation was performed for 5 minutes for the first stage, and in the second stage the same dosages of collector and promoter were added again. After conditioning for 5 minutes, flotation was further performed for 5 minutes.

Leaching tests

The leaching tests were carried out in a mechanically stirred 1 lt glass vessel. The overflow product obtained from hydrocyclone separation was used as feed material and leached at 10 %

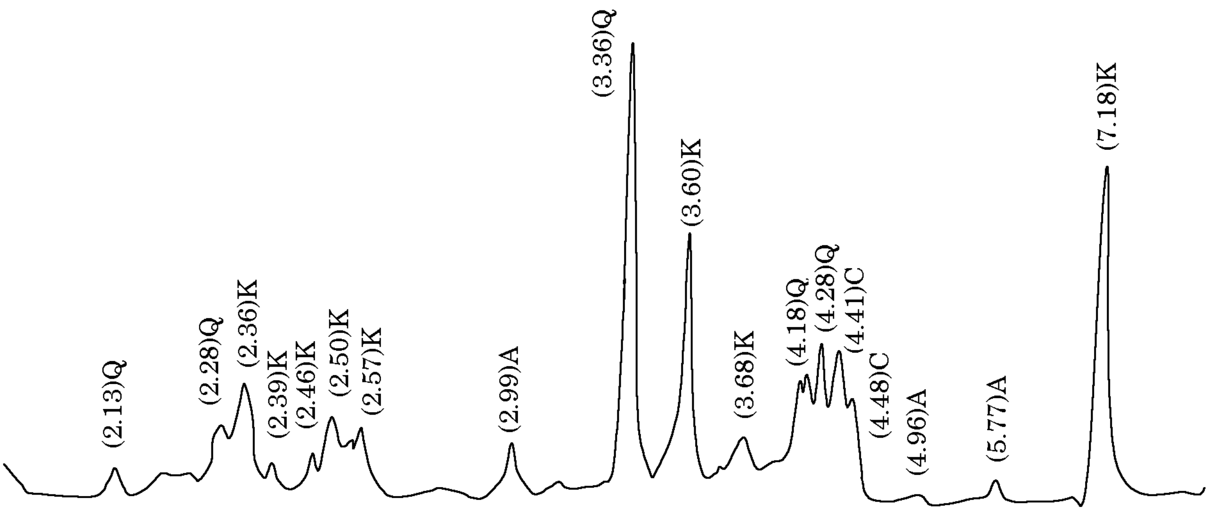

Figure 1: XRD pattern of İvrindi alunitic kaolin
Şekil 1 : İvrindi alunitli kaolinin XRD kırınımı

pulp density for 1 hour. Reagent grade H_2SO_4, HCl and Na_2CO_3 were used for pH adjustment.

Roasting tests

The roasting tests were carried out in a muffle furnace at temperatures ranging between 600-1100 °C for 1 hour. The roasted sample was then divided into two parts and one of them was leached in water for 1 hour to dissolve any soluble sulphur compounds formed during roasting. The structural changes in the roasted material were determined by X-ray diffraction analysis.

RESULTS AND DISCUSSION

Degritting and Classification Tests

Following degritting of the original sample, its particle size distribution was determined by wet sieving down to 38 µm and by Coulter Counter Industrial Model D for sub-sieve sizes. The particle size distribution of the sample is given in Figure 2.

Moreover, iron and sulphur contents of the sieve fractions were determined to find out their distribution with respect to particle size (Table 2). Results of particle size analysis and of chemical analysis of the sieve fractions revealed that almost 60 % of the original sample was finer than 38 µm, at finer sizes the sulphur content increased while the iron content decreased considerably.

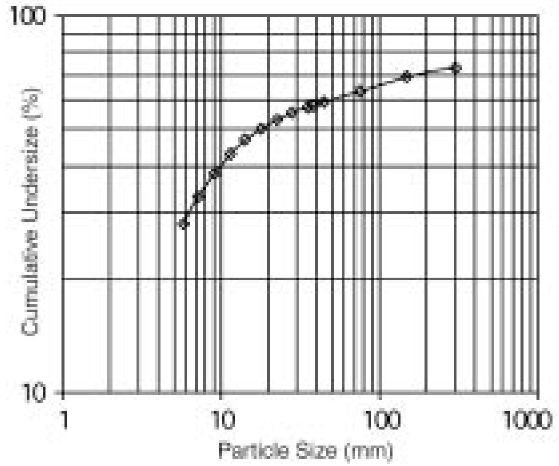

Figure 2: Particle size distribution of İvrindi alunitic kaolin
Şekil 2: İvrindi alunitli kaolininin tane boyu dağılımı

Table 2. Iron and sulphur contents of different particle size fractions of İvrindi alunitic kaolin
Çizelge 2. İvrindi alunitli kaolininin farklı tane boyu fraksiyonlarının demir ve kükürt içerikleri

Size (microns)	Weight (%)	Fe_2O_3 (%)	SO_3 (%)
+300	27.18	5.12	0.90
-300+150	4.29	3.10	0.83
-150+75	5.09	2.65	0.78
-75+45	4.26	2.18	0.78
-45+38	1.19	1.72	0.83
-38	57.99	1.92	1.28

Kaolins for ceramic productions are controlled generally in terms of iron contents, particle size distribution, strength and rheological properties (Harben, 1992; Patterson and Murray, 1983). Therefore, in the first step kaolin with suitable particle size distribution (<20 μm) should be produced. The original sample was degritted at 50 % pulp density for 10 minutes and screened through 300 μm sieve. The undersize material was then diluted to 20 % pulp density and fed to the hydrocyclone at 3.5 bar inlet pressure. The particle size distribution of the overflow product is given in Figure 3.

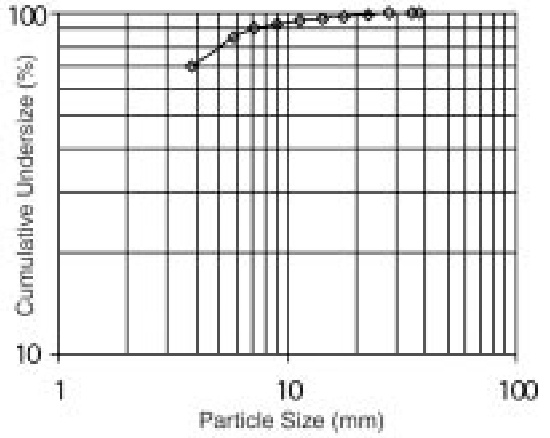

Figure 3: Particle size distribution of the cyclone overflow product

Şekil 3: Hidrosiklon üst akımının tane boyu dağılımı

Approximately 44 % of the hydrocyclone feed were taken as overflow product with particle size finer than 20 μm. Iron and sulphur contents of the hydrocyclone products showed that while iron content of the overflow decreased, its sulphur content increased with respect to the feed grade (Table 3).

Table 3. Iron and sulphur contents of cyclone products.

Çizelge 3. Hidrosiklon ürünlerinin demir ve kükürt içerikleri.

Product	Fe_2O_3 (%)	SO_3 (%)
Overflow	1.82	1.53
Underflow	2.68	0.85
Feed	2.31	1.14

In order to determine whether the sulphur content was due to alunite or adsorbed SO_4^{2-} ions on kaolinite particles at sub-sieve sizes, XRD analysis were done on +5.6 mm, -0.212 + 0.106 mm and –0.038 mm fractions. As can be seen from the XRD patterns given in Figure 4, alunite was identified only in –0.038 mm fraction, clearly proving that the origin of sulphur at sub-sieve sizes was alunite. Hence, it was concluded that most of the alunite grains were passed to the overflow product and it was impossible to obtain a final product with low sulphur content by only degritting and classification.

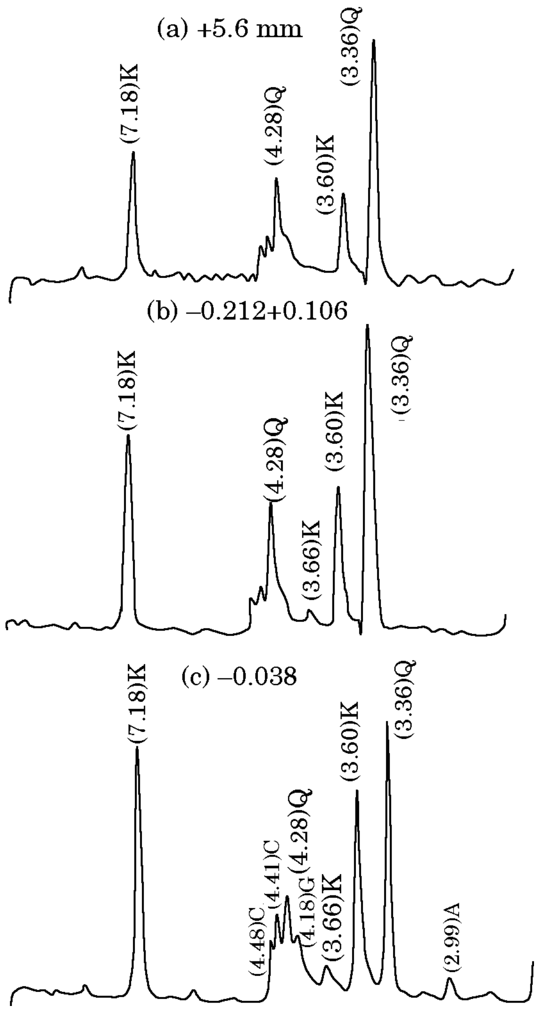

Figure 4: XRD patterns of some particle size fractions of İvrindi alunitic kaolin

Şekil 4: İvrindi alunitli kaolininin bazı tane boyu fraksiyonlarının XRD kırınımları

Flotation Test

The results of flotation test performed on the –0.038 µm fraction are reported in Table 4. As mentioned above, the flotation conditions optimised by Gebhardt et al. (1998) to obtain an alunite concentrate from low grade alunite dispersed very finely in the matrix of a quartz –kaolinite ore were employed to remove alunite from İvrindi alunitic kaolin. According to the results reported by Gebhardt et al. (1998), alunite could be removed with a recovery of 42 % with one flotation stage from an ore containing 1.6 % SO_3. The cumulative recovery after two consecutive flotation stages was increased to approximately 65 %. Although, İvrindi alunitic kaolin has similar mineralogical and chemical compositions, only 18.24 % of SO_3 could be removed after two stages of flotation (Table 4). The SO_3 content of kaolinite could only be reduced from 1.09 to 1.06 %.

Table 4. Results of alunite flotation test.
Çizelge 4. Alunit flotasyonu deney sonuçları.

Product	Weight (%)	SO_3 (%)	Recovery (%)
Float 1	4.87	1.40	6.27
Float 2	11.23	1.16	11.97
Concentrate	83.90	1.06	81.76
Feed	100.00	1.09	100.00

Comparison of the particle size analysis of both samples showed that İvrindi alunitic kaolin was finer than that of used by Gebhardt, et al. (1998). Hence, the difference in the flotation results of these two studies may be attributed to the difference in the fineness between the two samples and inefficient flotation of ultrafine particles by classical froth flotation method.

Leaching Tests

The leaching tests were executed to assess the influence of pH and pulp temperature on the dissolution behaviour of alunite in kaolin. The natural pH of the sample was around 7 - 7.5 with tap water. In the first step, sulphuric acid was used for pH regulation. The results of leaching tests carried out under different pH and temperatures are summarised in Table 5.

Table 5. Results of leaching tests carried out under different pH and temperatures
Çizelge 5. Farklı pH ve sıcaklıklarda gerçekleştirilen liç deneylerinin sonuçları

	pH	SO_3 (%)
Cold Leaching	7-7.5	1.20
(15-20 °C)	2-2.5	1.65
Hot Leaching	7-7.5	1.12
(60-65 °C)	2-2.5	1.73
Feed		1.53

Sulphur content of the sample was slightly reduced at neutral pH and the effect of hot leaching was negligible. However, the sulphur content was increased to higher values than that of feed sample at acidic pH, in spite of successive washings with clean water. This unexpected result was attributed to reprecipitation of varieties of hydroxysulphates containing K, Al and Fe ions dissolved from the sample during sulphuric acid leaching (Figure 5). The Eh-pH diagram of Al-K-S-H_2O system at 25 °C drawn by using Outokumpu HSC Chemistry software showed that precipitation of alunite $[KAl_3(OH)_6(SO_4)_2]$ is favoured between pH 2.3-7. When the temperature of the solution is increased to 65 °C, the stability region of alunite broadens down to pH 0 (Figure 6). The slight increase in the sulphur content of the sample leached at 65 °C was in agreement with broadening of the stability region of alunite.

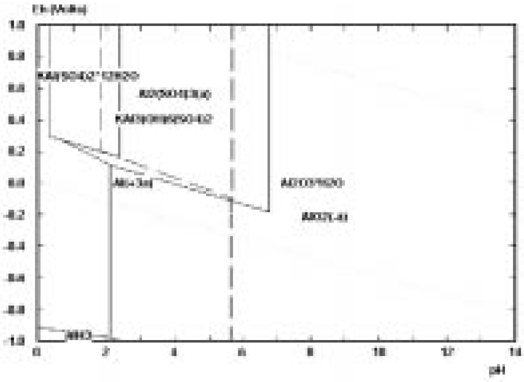

Figure 5: Eh-pH diagram of Al-K-S-H_2O system at 25 °C (dashed lines show the aqueous phase)

Şekil 5: Al-K-S-H2O sisteminin 25 °C sıcaklıkta Eh-pH diagramı (kesikli çizgi sulu fazı göstermektedir)

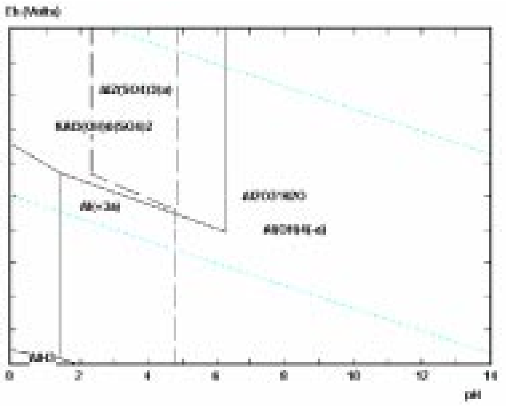

Figure 6: Eh-pH diagram of Al-K-S-H_2O system at 65 °C

Şekil 6: Al-K-S-H2O sisteminin 65 °C sıcaklıkta Eh-pH diagramı

Dissolved iron ions in the solution may be found in aqueous form of $FeSO_4$(a), Fe^{2+}(a) and $FeSO^+_4$ (a) or in solid precipitate form of $FeSO_4$, Fe_2O_3 and FeS_2 depending on pH and Eh of the solution and the amount of iron ions dissolved (Figure 7). Precipitation of jarosite $[KFe_3(SO_4)_2(OH)_6]$ may also be possible. However, considering slow kinetics of jarosite precipitation and requirement of several hours and high temperatures (100 °C) for complete precipitation (Das et al., 1996), jarosite precipitation may be in negligible amount in the experimental conditions of this work (65 °C and 1 hour leaching time). Detailed leaching tests should be undertaken to reach certain conclusions about re-precipitation of alunite and jarosite in the solution.

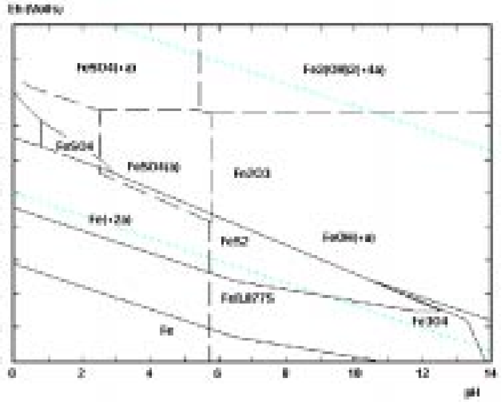

Figure 7: Eh-pH diagram of Fe-S-H_2O system at 65 °C

Şekil 7: Fe-S-H2O sisteminin 65 °C sıcaklıkta Eh-pH diagramı

In order to prevent re-precipitation of alunite, redox potential of the pulp was decreased to reducing potential region (< 0 mV) by using a strong reducing agent, sodium dithionite. Since, the stable form of sulphur is H_2S(a) in highly acidic and reducing conditions (Pourbaix, 1966), formation of hydroxysulphates in the solution was not expected. When the sample was leached in the presence of sodium dithionite at pH 2-2.5 and 15-20 °C temperature, the SO_3 content was decreased to 1.32 % after and to 1.24 % after 60 minutes leaching. The results of the tests showed that the increase in the sulphur content of the sample was prevented in reducing conditions, but negligible amount of sulphur could be removed even in highly acidic solutions.

When H_2SO_4 was replaced by HCl, sulphur content of the sample was decreased from 1.53 to 1.04 % SO_3 at a pH of 2-2.5 and 60-65 °C pulp temperature. This was due to formation of $AlCl_3$(a), K^+(a) and Fe^{2+}(a) in acidic solutions rather than hydroxysulphate precipitation. Although this value is lower than that obtained by hot leaching with H_2SO_4 (1.24 % SO_3), it is still far from the acceptable value (0.5 % SO_3).

Alkaline leaching was carried out as an alternative to acid leaching. Pulp pH was adjusted to 12-13 by using Na_2CO_3 and the temperature was maintained at 60-65 °C. Since, the sulphur dissolved is in the form of SO_4^{-2} and precipitation of alunite is no longer possible in alkaline solutions (see Figure 6), the sulphur content of the sample was decreased to 0.75 % SO_3 by leaching with Na_2CO_3.

Roasting Tests

The effect of roasting and leaching after roasting on the reduction of the sulphur content of the sample was illustrated in Figure 8. The sulphur content was decreased slightly between 600 and 800 °C. However, it was rapidly decreased after 800 °C and a product with 0.48 % SO_3 was obtained at 1000 °C. The sulphur was completely removed from the sample probably in the form of SO_2 and/or SO_3 gas. Leaching of roasted sample slightly reduced the sulphur content and this reduction was negligible at high temperatures.

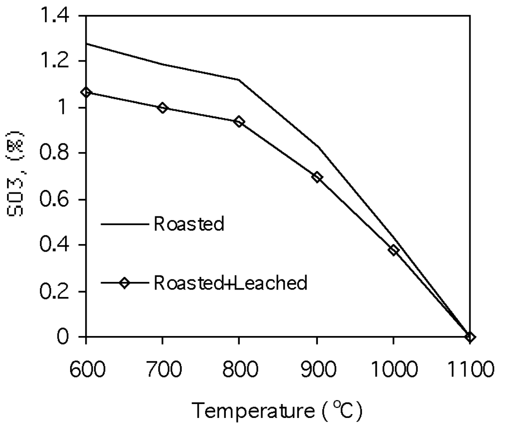

Figure 8: Effects of roasting and leaching after roasting on reduction of sulphur content
Şekil 8: Kavurma ve kavurma sonrasında liç işlemlerinin kükürt içeriğindeki azalmaya etkileri

Structural variations of kaolinite were determined by X-ray diffraction. The XRD patterns of the roasted samples are given in Figure 9. Kaolinite structure is destroyed starting from 600 °C and changes to metakaolin. Between 700 and 1000 °C temperatures, only quartz peaks were determined. With this change to metakaolin the sample also loses its plastic properties when mixed with water. However, it is known that metakaolin can be rehydrated by extended exposure to water to again form kaolinite and thus, to regain its plastic property (Lawrence, 1972). Hence, the roasted samples were leached with water both to remove any water soluble sulphur species formed during roasting and to regain their plastic property.

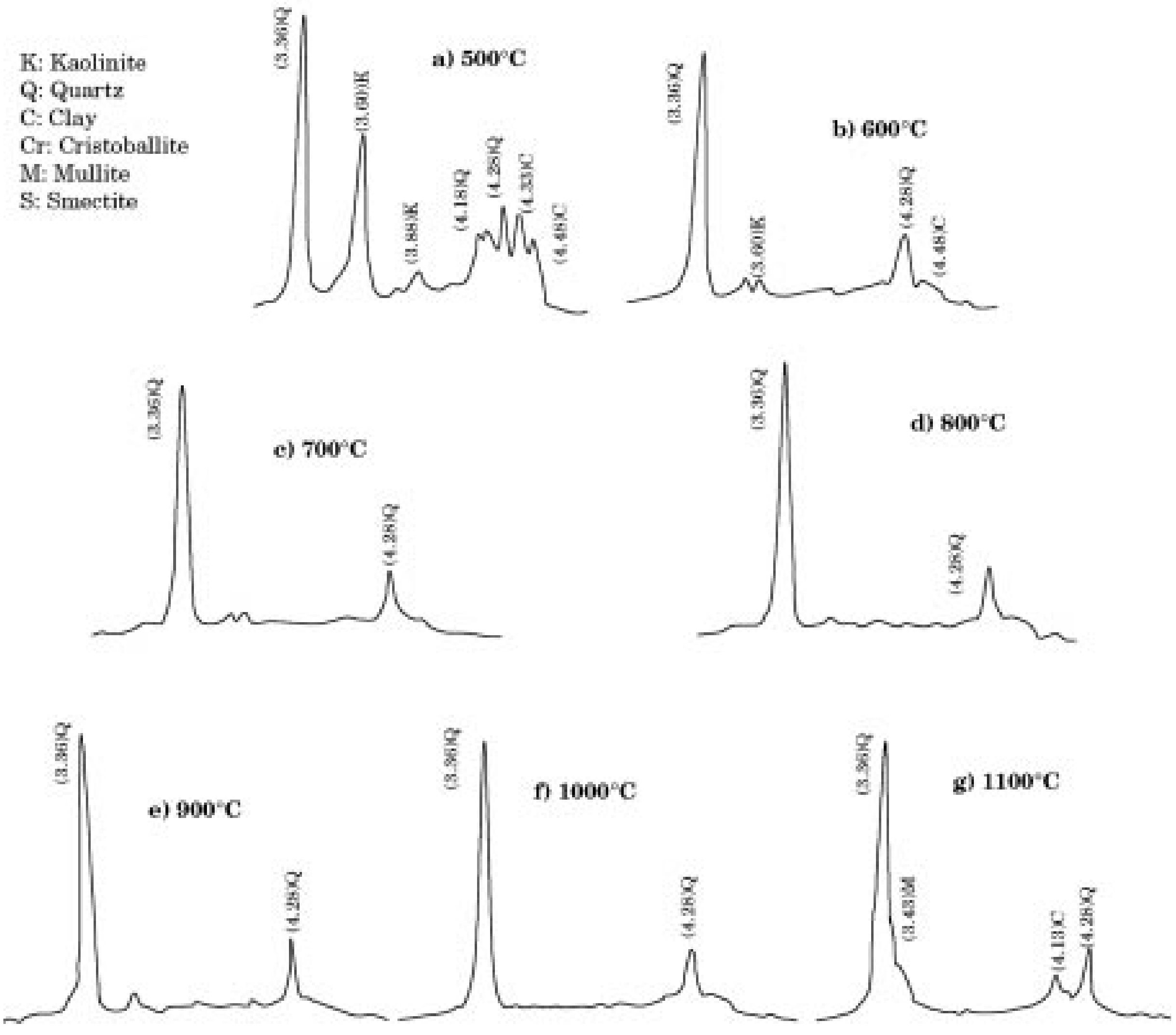

Figure 9: XRD patterns of roasted samples at different temperatures
Şekil 9 : Farklı sıcaklıklarda kavrulmuş numunelerin X-ışını kırınımları

However, XRD patterns of the leached samples after roasting were the same as the only roasted samples. Hence, it was concluded that kaolinite structure could not be restored even after 1 hour leaching of the roasted sample in water. At temperatures higher than 1000 °C, kaolinite was transformed into mullite and cristoballite phases.

Although sulphur content and brightness of the sample was increased by roasting at 1000 °C, the plasticity in casting, which is one of the most important controlling parameter in ceramic production, disappeared owing to the fact that transformation of kaolinite structure into other phases.

CONCLUSIONS

Separation of alunite from kaolinite by degritting and classification was not possible since most of alunite grains were also merged to the overflow product together with kaolinite grains. This separation was also not possible by froth flotation due to inefficiency of this method at ultrafine particle sizes.

Sulphur content of the alunitic kaolin sample could be decreased down to 0.75 % SO_3 by leaching with Na_2CO_3. Leaching in acidic solutions, even in strongly reducing potentials, was not successful due to formation of solid phases [$KAl_3(OH)_6(SO_4)_2$ and $KAl(SO_4)_2.12H_2O$] at the experimental conditions.

Roasting was considered to be an alternative method to decrease sulphur content of the sample. However, the sulphur content could be reduced down to 0.5 % SO_3 by raosting at temperatures as high as 1000 °C. Since kaolinite was decomposed and its casting property was diminished, roasting at high temperatures was considered to be inapplicable.

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