Gümüşhane University Journal of Science

GUFBD / *GUJS* (2024) 14(1): 15-28 doi: 10.17714/gumusfenbil.1360601 Research Article

Exploring the utilization potential of kaolin in the Balıkesir Sındırgı region

Balıkesir Sındırgı bölgesi kaolinlerinin kullanım potansiyellerinin incelenmesi

İlker ERKAN*[,1], **İbrahim ALP**[2]

[1] Gümüşhane Üniversitesi Mühendislik ve Doğa Bilimleri Fakültesi Maden Mühendisliği Bölümü, Gümüşhane
[2] Karadeniz Teknik Üniversitesi Maden Mühendisliği Bölümü, Trabzon

• Received: 14.09.2023 • Accepted: 18.10.2023

Abstract

Natural kaolins may contain some metal cations (K^+, Na^+, Mg^{+2}, Ca^{+2}) and anions such as carbonate, phosphate, and sulfate as impurities, depending on the formation conditions. The kaolins of Turkiye generally give a high-quality white color after firing due to their low Fe_2O_3 content. Unfortunately, Turkiye's kaolin deposits generally contain high levels of SO_3. Since the alunite mineral, which is the source of SO_3, cannot be removed from the structure by known methods, kaolins containing alunite can only be used in the white cement sector. In this study, the suitability of the kaolins of the Balıkesir Sındırgı region, which has a large part of the kaolin reserves of Turkiye, to the areas of use where kaolin is mostly used in its current state has been investigated, and the samples obtained from the region have been examined in which areas of use they are suitable for use in raw form, and suggestions have been made about the enrichment methods to be carried out by comparing with the studies in the literature.

Keywords: Alunite, Enrichment, Kaolin, Removal

Öz

Kaolinler, jeolojik oluşum süreçlerine ve koşullarına bağlı olarak safsızlık olarak metal katyonları (K^+, Na^+, Mg^{+2}, Ca^{+2}) ve anyonlar (karbonat, fosfat ve sülfat gibi) içerebilirler. Genellikle düşük olan Fe_2O_3 içeriği sayesinde Türkiye'deki kaolinler pişirildikten sonra yüksek beyazlığa sahip olmaktadırlar. Ancak Türkiye kaolin yataklarının büyük bir bölümünde kükürt içerikleri yüksektir. SO_3 kaynağı olan alunit mineralinin bilinen yöntemlerle bünyeden uzaklaştırılamaması nedeniyle alunit içeren kaolinler sadece beyaz çimento sektöründe kullanılabilmektedir. Bu çalışmada Türkiye kaolin rezervinin büyük bir kısmına sahip olan Balıkesir Sındırgı bölgesi kaolinlerinin mevcut halleri ile kaolinin en fazla kullanıldığı kullanım alanlarına uygunluğu araştırılmış ve bölgeden temin edilen örneklerin ham olarak hangi alanlarda kullanıma uygun olduğu incelenmiş ve literatürde yapılan çalışmalar ile kıyaslanarak yapılması gereken zenginleştirme yöntemleri ile ilgili önerilerde bulunulmuştur.

***Anahtar kelimeler**: Alunit, Zenginleştirme, Kaolin, Uzaklaştırma*

---

* İlker ERKAN; ilkererkan@gumushane.edu.tr

1. Introduction

Kaolin is the name given to a group of clay minerals within the classification of clay minerals. Kaolinite ($Al_2Si_2O_5(OH)_4$) is known as the most important mineral of the group, and halloysite, nacrite, and dickite are the other minerals of the group. Kaolinite is a clay mineral with a hydro silicate aluminum composition (Demirbilek, 2007). The term kaolin refers to kaolin types and kaolinitic clays formed in various crystal structures (DPT, 1995). The kaolin clay group, the main mineral of which is kaolinite, is formed as a result of the decomposition of feldspar-rich igneous rocks. Kaolin was first discovered by a Chinese named "Kau-Ling" in the Jiangxi region of China in 3000 BC, and the name of the discoverer was given as the name of the rock (Ece & Yuce, 1999). In many sources in the literature, clay and kaolin are used interchangeably.

Kaolin is defined as a soft clay with a grain size smaller than 2 µm, white color, plasticity, and softness. Kaolin has a density of 2.62 g/cm^3 and a hardness value of 1.5-2 according to Mohs hardness. The compounds sought and desired in the chemical analysis of kaolin are: Al_2O_3, SiO_2, Fe_2O_3, TiO_2, MgO, CaO, K_2O, and Na_2O. The amounts of compounds and their mineralogical, physical, and chemical properties play an important role in the classification of kaolin. An ideal kaolin consists of 46.5% SiO_2, 39.5% Al_2O_3, and 14% H_2O. However, in cases where aluminum, which is the most important element and the main constituent, is reduced, low amounts of iron, sulfur, and potassium (K_2O) enter the structure. The presence of K_2O indicates the presence of some alunite, which is undesirable because it causes an increase in the superheat loss in heat treatment (Ece & Yüce, 1999; Güneş et al., 2009).

Kaolin is also a unique raw material due to its chemical properties. The plasticity feature, which is especially preferred in the ceramic industry, is a feature that is not found in any other mineral.

1.1. Usage areas of kaolins

Approximately 36 million metric tons of kaolin are produced annually around the world. Kaolin is an important raw material with many uses depending on its physical and chemical properties. Kaolin can be used in many industrial fields according to its whiteness, brightness, viscosity, film strength, degree of crystallization, and hiding power. The usage areas of kaolin can be listed as the paper industry, ceramics, paint, and plastics. In addition to these areas, it is used in ink production because it provides gloss preservation, in the tire industry because it has a cost-reducing and strengthening effect, in glass fiber production because it provides heat insulation, and in the production of plastics because it increases strength. It is also used in water-based adhesives due to its ability to increase fluidity, in the production of automobile and metal polishers for cleaning oxidized surfaces, in the production of toothpaste and in the production of some drugs due to its absorption properties. It is also important for the ceramic and paper industries, as it is the basic raw material for these fields.

The kaolin produced in Turkey is mostly (80%) consumed in the cement industry. The remaining 20% of the kaolin produced is consumed in ceramics, glass, paper, and other sectors. When the ratios according to the consumption sectors are analyzed, it is understood that kaolin produced in Turkey is consumed in its raw form without any processing. In Europe and America, on the other hand, 75% of the kaolin produced in raw form is used in facilities to produce paper and fine ceramics. This fact makes it obvious that the paper and kaolin industries are very developed in these countries (Güneş et al., 2009). Kaolin is the most preferred raw material after cellulose because it can be used as filler in the paper industry and in the production of glossy paper. While quartz mineral is not desired in kaolin to be used in the paper industry, kaolinite mineral with 90-100% purity is sought. In addition, the brightness should be at least 85%, and the 80% of the grain size should be less than 2µm and the Brookfield viscosity value should be less than 7000 cps. Kaolin regulates paper appearance properties such as gloss, smoothness, and lightfastness. Iron oxide and titanium oxide minerals are the impurities that reduce the brightness of kaolin the most (Çiftlik, 2010). The chemical properties required for kaolin used as filler and coating in the paper industry are shown in Table 1 (Çiftlik, 2010; DPT, 2001).

The kaolin to be used in the ceramic industry is required to be dispersible in water, to have good plastic properties and low firing shrinkage, and to have a white color after firing. The most consumed areas of kaolin in the ceramic industry are porcelain, refractory and coating bricks, sanitary installations, wall tiles, and insulators. Since pure kaolin melts at 1760 °C, it is preferred that the kaolin to be used in this sector contain

75-80% kaolinite minerals. Also, white firing color, high resistance to abrasion, low viscosity, and very low Fe_2O_3 and TiO_2 ratios are desired in these kaolins (Table 2) (DPT, 2001).

Table 1. Chemical properties of kaolin used in paper industry (DPT, 2001)

Compound	Filler kaolin (%)	Coating kaolin (%)
Al_2O_3	24-41	34-41
SiO_2	45	
CaO	<1	
MgO	<1	
Fe_2O_3	<0.5	
SO_3	Max 1	
Whiteness	>80	
Wear loss	50 mg	15 mg

Table 2. Kaolin standard used in ceramic industry (DPT, 2001)

Compound	%
SiO_2	59.5-73
Al_2O_3	19.0-28.0
Fe_2O_3	0.5-1.0
TiO_2	0.3-0.4
CaO	0.1-0.2
MgO	0.1-0.2
K_2O	0.1-0.3
Na_2O	0.1-0.3
Whiteness	88-90
SO_3	Max 0.2

Calcined and non-laminated kaolin with a mineral structure is used with ground calcite powder, titanium oxide, and talc in water-based interior plastic and latex paints, exterior paints, and oil-based paints, especially industrial paints. In semi-gloss and glossy water-based paints, 98% of kaolins larger than 2 µm are used, while these paints contain between 50% and 70% pigment. In latex paints, the kaolins used should provide good coverage and have refractive index values close to the refractive indices of the binders used in paint production (>1.50) (Tunçay, 2006). The chemical content values that kaolins to be used in the paint industry should provide are shown in Table 3 (Çiftlik, 2010).

Table 3. Chemical properties of kaolin used in paint industry (DPT, 2001)

Compound	%
Al_2O_3	Min 38.8
SiO_2	Max 45.2
TiO_2	0.6-1.7
CaO	Max 0.02
Fe_2O_3	0.3-0.9
MgO	0.03-0.05
Na_2O	0.05-0.3
K_2O	0.05-0.2
Brightness	79-82

Kaolin is widely used in the cement industry, and 30% of the total raw ore produced in Turkey is consumed in this field. The chemical content values that kaolin to be used in the cement industry should provide are shown in Table 4 (Çiftlik, 2010).

Table 4. Kaolin standards used in cement industry (DPT, 2001).

Compound	%
SiO_2	51-67.5
Al_2O_3	22-29
Fe_2O_3	Max 0.4
TiO_2	0.4-0.5
CaO	Max 0.1
MgO	Max 0.1
K_2O	0.5-2.0
Na_2O	0.3-0.4
SO_3	Max 1

1.2. Status of kaolin in Turkiye

Since the kaolin deposits in Turkiye have similar geological formation structures, almost all of them are of hydrothermal origin. According to the studies carried out by the General Directorate of The Institute of Mineral Research and Exploration (M.T.A.), the kaolin reserves of Turkiye are over 100 million metric tons, but the amount of operable reserves is around 36 million metric tons. The distribution of Turkiye's kaolin reserves according to their locations is shown in Table 5.

Table 5. Kaolin deposits, grade, usage areas and reserves of Turkiye (DPT, 2001).

Location	Al_2O_3 (%)	Usage area	Reserve (proved+ estimated) (Tons)	Mineable reserve (proved) (x1000 Ton)
Balıkesir-Sındırgı	13-33	Fine ceramic, tile, refractory, paper	70000000	25000
Balıkesir-Ayvalık	15-32	Ceramic and tile, glazed tile	1000000	500
Balıkesir-İvrindi	20-31	Fine ceramic and tile, glazed tile	970000	500
Balıkesir-Gönen	23-28	Ceramic	150000	50
Çanakkale-Çan	17-35	Ceramic and refractory	5000000	2000
Bursa-Kemalpaşa	20-24	Paper	1000000	1000
İstanbul-Arnavutköy	15-35	Refractory	800000	-
Eskişehir-Mihalıççık	20-33	Ceramic and tile, glazed tile	3330380	1000
Bilecik-Söğüt	15-23	Ceramic	1000000	500
Kütahya-Gevrekseydi	20-24	Paper	724924	200
Kütahya-Altıntaş	20-31	Ceramic, tile, glazed tile, paper	1206000	500
Kütahya-Emet	20-30	Ceramic, tile, glazed tile	1070286	100
Kütahya-Simav	20-24	Ceramic, tile, glazed tile	370000	100
Uşak-Karaçayır	11-21	Ceramic, tile, glazed tile	800000	500
Kayseri-Felahiye	23-34	Ceramic and refractory	450000	20
Konya-Sağlık	15-30	Tile, glazed tile, ceramic	607000	100
Nevşehir-Avanos	18-33	Ceramic, electro porcelain, tile	1277000	100
Niğde-Aksaray	15-32	Tile, glazed tile, paper	1500000	1000
Trabzon-Araklı, Arsin	14-23	Tile, glazed tile	200000	50
Rize-Ardeşen, Fındıklı	14-23	Tile, glazed tile	275000	50
Giresun-Bulancak	12-24	Tile, glazed tile	7785000	2000
Ordu-Ulubey	17-23	Paper	730000	100
Others				700
Total			100245590	36020

Sındırgı district of Balıkesir is the region with the largest known hydrothermal kaolin deposits in Turkey. The kaolin deposits in this region are endogenous, volcano-sedimentary deposits were formed as a result of hydrothermal alterations. This region is also important because it contains kaolin with alunite, which is undesirable in kaolins used in the ceramic industry due to the outgassing and alkaline sulfate evaporation occurring in the firing of Sındırgı kaolins at high temperatures, and porous structures, cracked structures, and fractures that occur in ceramics caused by a noncompleted sintering process. The kaolin (+/- alunite) formations here were formed as a result of hydrothermal alteration of rhyolite-riodacite tuffs. These tuffs consist of alkali feldspar, quartz, biotite, and muscovite minerals, and pumice fragments.

Sulfur and iron contents in the alunitic kaolins in this region are the most important impurities that deteriorate the raw material's quality. According to the grain size distribution and grain size range, when the iron and sulfur contents are taken into consideration, it has been determined that iron accumulates in coarse grain sizes and sulfur accumulates in fine grain sizes; therefore, alunite grains are found in fine grain sizes together with kaolinite (Demirtaş, 2011).

The fact that the kaolin reserves in our country cannot be used in the required areas for such reasons also has an impact on the national economy. For this reason, the import and export data of kaolin obtained from the Turkish Statistical Institute for Turkey have been analyzed in detail and shown in Table 6 (TUİK, 2020).

Table 6. Kaolin import and export data of Turkiye (organized from TUİK, 2020)

		Import		**Export**	
	Product name	**Amount, kg**	**Dollar, $**	**Amount, kg**	**Dollar, $**
2016	Kaolin; raw	183404647	14619349	34398136	1010578
	Kaolin; other	128728204	25454798	328054	91940
	Raw clays with kaolin	28363824	3540337	32442530	1052562
	Grounded kaolin clays	15915626	4028311	225103	105145
	Total	**356412301**	**47642795**	**67393823**	**2260225**
2017	Kaolin; raw	183172762	14969289	122035725	3384078
	Kaolin; other	170748066	31850972	497416	273715
	Raw clays with kaolin	22112094	2684761	19032038	651607
	Grounded kaolin clays	19625262	4062608	126891	52796
	Total	**395658184**	**53567630**	**141692070**	**4362196**
2018	Kaolin; raw	197013959	19867635	89885972	2775026
	Kaolin; other	134959313	27840715	501579	260337
	Raw clays with kaolin	31049679	3834970	1115275	122497
	Grounded kaolin clays	18673180	3865921	123802	45718
	Total	**381696131**	**55409241**	**91626628**	**3203578**
2019	Kaolin; raw	155152367	15572422	189498562	5090890
	Kaolin; other	104225122	22946331	525697	27375
	Raw clays with kaolin	18505356	2508130	750085	176399
	Grounded kaolin clays	16793926	3377944	197741	81403
	Total	**294676771**	**44404827**	**190972085**	**5622442**

According to these data, the difference between the foreign exchange spent for the import of kaolin and kaolin-containing clays and the foreign exchange earned from exported products is clearly visible between 2016 and 2019. The point to be noted here is that most of the income obtained from exports is obtained from the unprocessed raw form of kaolin.

2. Characterization and identification of kaolin samples

In order to investigate the suitability of four different raw kaolin samples obtained from the Balıkesir Sındırgı region. Geographic information systems are very effective sources for geo-location maps (Yılmaz & Günen, 2023). The geo-location map prepared with QGIS open-source software is shown in Figure 1. For the areas where kaolin is most commonly used, a series of characterization studies were carried out to clearly understand the structure of these samples. In the density determination studies, the average density of the samples was determined to be 2.45 g/cm^3, and this value suggested that there is a mineral with a lower density than kaolinite in the structure. X-ray diffractometer (XRD) analyses of the samples (Figure 2) showed the presence of opal (2.09 g/cm^3) together with kaolinite (2.75 g/cm^3), alunite (2.74 g/cm^3), and quartz (2.65 g/cm^3), and it was concluded that the reason for the low density measured was the presence of opal.

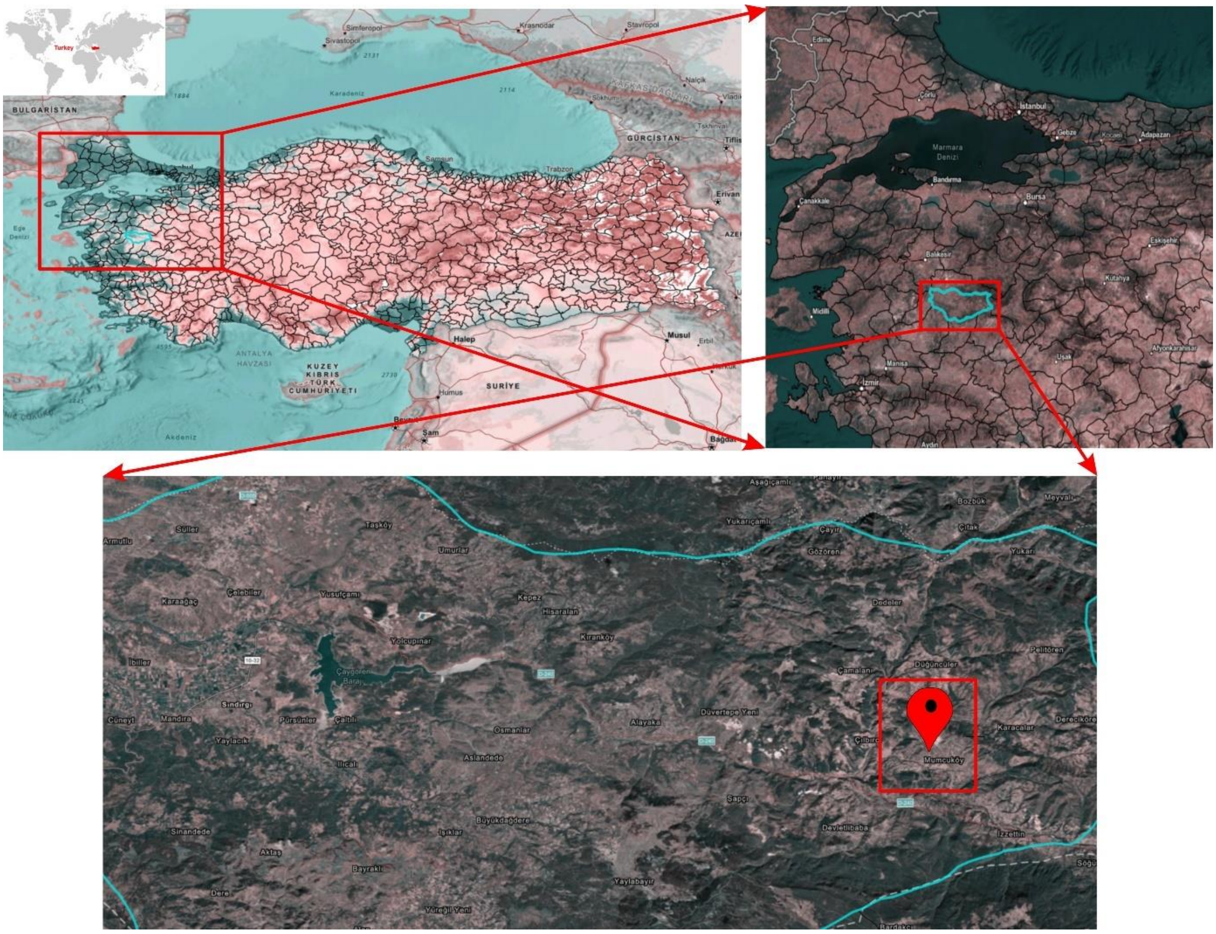

Figure 1. Site location map of the obtained samples

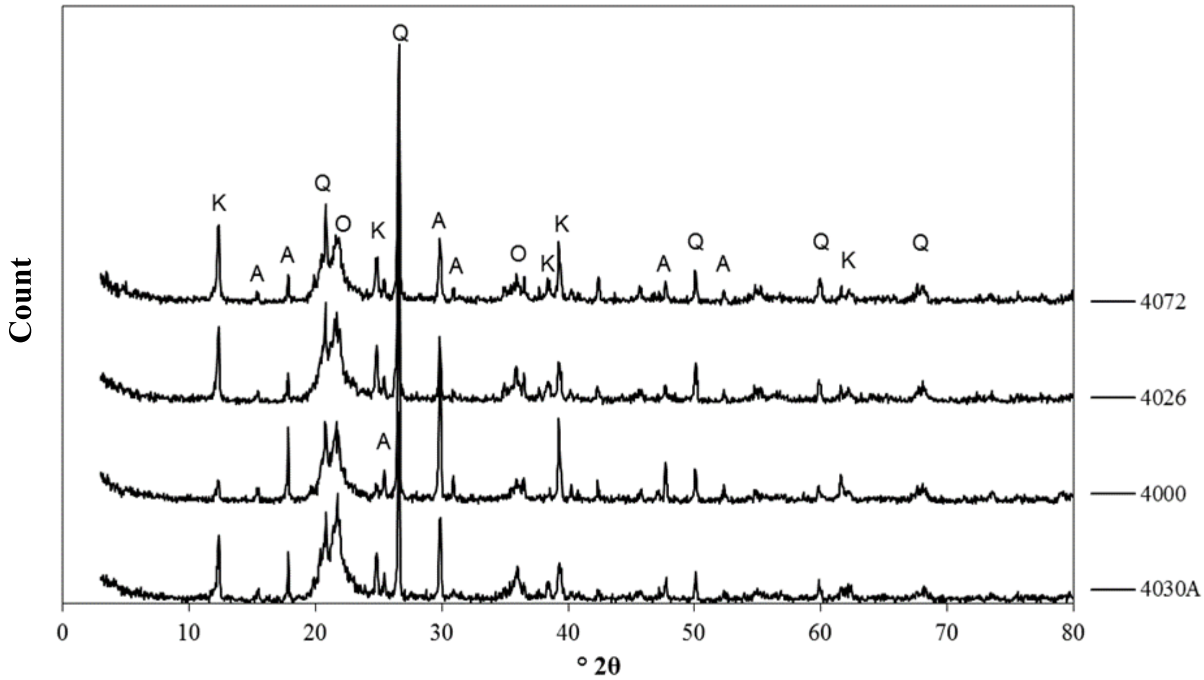

Figure 2. XRD graphs of raw samples (K: kaolin; Q: quartz; A: alunite; O: opal)

XRD analyses were carried out on a RigakuD/max-IIIC XRD in a measurement range of 3-80° 2θ, with reading steps of 0.02° 2θ at a measuring speed of 3°/min and in a CuKα (1.54Å) radiation medium. The analyses determined that the samples generally contain kaolinite, quartz, opal, and alunite minerals. Since the densities of kaolinite (~2.75 g/cm^3), quartz (~2.65 g/cm^3), and alunite (~2.74 g/cm^3) minerals are close to each other, it is thought that the presence of opal detected in the structure causes the measured average density of the samples (2.45 g/cm^3) to be low due to the low density of opal (~2.09 g/cm^3).

In the literature studies on the region, it was revealed by XRD studies that kaolins in Balıkesir-Sındırgı region have similar mineral contents (Yılmaz, 2008; Ekinci, 2009; Demirtaş, 2011; Tatar, 2012).

In the XRD graphs obtained (Figure 1) for the alunite mineral, 4.95 Å (17.8° 2Θ), 3.48 Å (25.5° 2Θ), 2.98 Å (29.8° 2Θ), 1.89 Å (47.7° 2Θ) peaks for the alunite mineral, 7.2 Å (12.34° 2Θ), 3.57 Å (24.8° 2Θ), 2.34 Å (38.36° 2Θ) peaks for the kaolinite mineral, peaks of 4.26 Å (20.83° 2Θ), 3.35 Å (26.6° 2Θ), 1.82 Å (50.1° 2Θ), 1.54 Å (59.87° 2Θ) are characteristic for the quartz mineral, and peaks of 4.05 Å (21.745° 2Θ), 2.48 Å (36° 2Θ) for the opal mineral.

XRD results showed that the samples are kaolinite-containing alunite minerals. Literature studies also confirm this finding (Ekmekçi et al., 2001; Özdemir & Çetişli, 2005b; Yılmaz, 2008; Ekinci, 2009; Demirtaş, 2011; Tatar, 2012). The quartz mineral is dominant in all of the samples. In addition to quartz minerals, opal, another SiO_2 source, is also observed in the analyses. Quartz, which is the most abundant mineral in each sample, is most abundant in sample 4026 and least abundant in sample 4000. In the other two samples, quartz is found in close ratios to each other. Among the samples, the one containing the most alunite mineral was the sample named 4000, while the one containing the least alunite mineral was the sample named 4026. The sample named 4030A contained the second highest amount of alunite mineral. The richest sample in terms of kaolinite mineral content was sample 4072, and the poorest sample was sample 4000. Sample 4030A was the second-poorest sample in terms of kaolinite.

Chemical analyses were also carried out to determine the basic oxide compounds and superheat losses (LOI) of the samples. Chemical analyses were carried out by the X-ray fluorescence method (XRF), and the results are shown in Table 7.

Table 7. Results of chemical analyses of raw samples

Sample code	%									
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2	SO_3	K.K.
4000	65.2	13.93	1.04	0.11	0.03	0.07	2.74	0.23	9.189	15.96
4026	72.8	14.89	0.24	0.11	0.03	0.05	1.05	0.29	3.546	9.98
4030-A	70.0	15.02	0.47	0.12	0.03	0.05	1.48	0.30	4.869	11.59
4072	68.7	16.91	0.66	0.13	0.05	0.05	1.39	0.30	4.469	11.67

According to the results of the chemical analyses (Table 7), in which the basic oxide compounds and glow losses (LOI) of the samples were determined, the SO_3 and K_2O compounds observed in the samples are obvious indicators of the alunite structure. XRD analysis results also show that the amounts of SO_3 and K_2O compounds observed in the chemical analysis results coincide with the amounts of alunite. The presence of K_2O here may also be due to K-feldspar, which is present in small amounts in the structure (Ece & Ekinci, 2009).

Since the region where kaolin samples were obtained is a region formed as a result of volcano-sedimentation and consists of rhyodacitic and dacitic rocks, K-feldspar and plagioclase minerals are dominant. Geological studies conducted in the region also support the presence of the mentioned minerals. According to Ece & Ekinci (2009), who cited Akdeniz & Konak (1979) in their study, the area is known as the Akdağ Volcanics and Civanada Tuffs, and these volcanites are made up of lavas with the mineralogical compositions of rhyolite, dacite, rhyodacite, and andesite. In addition, Ekinci (2009), quoting Oygür (1997), stated that the epithermal mineralization in Mumcu (Balıkesir-Sındırgı) developed on faults cutting the Simav Graben vertically between Palaeozoic-aged metamorphics and Miocene-aged andesitic volcanics, and Elmacı (1989) stated that the Balıkesir-Sındırgı-Düvertepe region consists of Mesozoic-aged complex series from bottom to ceiling. He stated that it consists of Cenozoic aged basal tuff, basal opal, kaolin, ceiling opal, dacite tuff, clayey limestone-tuff, sandy kaolin, opal, pumice rhyolitic tuff, glassy rhyolitic lava, and rhyolite lava units.

Accordingly, the sources of CaO, MgO, and Na_2O compounds seen in chemical analyses are thought to be orthoclase, albite, biotite, and hornblende, which are members of these mineral groups.

In addition, the presence of quartz and opal was also revealed in the mentioned studies. These minerals are the main sources of SiO_2 seen in the analyses. However, SiO_2 is also present in the structure of many minerals. Among these, kaolinite and K-feldspar are the most basic minerals found in the samples. The high silica contents in the samples may be due to quartz, opal, K-feldspar, and non-kaolin clay minerals, or other non-clay minerals.

Al_2O_3 observed in the analyses indicates alunite, kaolinite, and K-feldspar structures. In most of the different studies in the literature, Fe_2O_3 content indicates iron minerals, which are frequently found with kaolin (Veglio et al., 1993; Veglio et al., 1996; Veglio 1997; Veglio et al., 1998; Ambikadevi & Lalithambika, 2000; Saikia et al., 2003; Calderon et al., 2005; Lee et al., 2006; Arslan & Bayat, 2009; Ciftlik, 2010), while iron minerals are not observed in any of the chemically analyzed samples. Bayraktar et al. (1999), stated in a study that the source of iron in alunitic kaolins of Balıkesir region is iron hydroxide plastered on the surfaces of goethite and kaolin grains (Bayraktar et al., 1999). In addition, Ece & Ekinci (2009) reported that jarosite, goethite, and Fe-hydroxyls were found as iron sources in the mineralogical composition of Sındırgı-Düvertepe kaolins. They determined that kaolinite, quartz, and alunite were the main minerals in the XRD analyses they applied to the kaolins obtained from the region, but they did not find any indication of iron minerals in the XRD analyses. This indicates that the amounts of iron minerals are too small to be seen in XRD analyses. In another study conducted with kaolins from Sındırgı region, Oygür (1997) mentioned the presence of biotite as a source of iron minerals. These findings also confirm the low Fe_2O_3 content of the samples in the chemical analyzes given in Table 7.

Analysis of the glow loss values reveals that they are parallel to the SO_3 values; the glow loss is higher in samples with higher SO_3 contents than it is in samples with lower SO_3 contents. The reason for this is that the glow loss measurement is performed above the decomposition temperature of SO_3 in the structure, and when these temperatures are reached, there is a loss due to the removal of SO_2 from the structure in the form of gas. In addition, the H_2O content in the structure is another factor affecting the glow loss values.

When compared with kaolins found in other regions of our country, it is seen that the alunite kaolins found in the Bursa-Mustafakemalpaşa region have similar SO_3 contents, but when the Al_2O_3 contents of the kaolins in the same region are taken into consideration, it is seen that they are very poor in terms of Al_2O_3 contents, and conversely, they are very rich in terms of SiO_2 contents (Özdemir & Çetişli, 2005a). However, these kaolins need to go through enrichment stages in order to be used in ceramic production. It has been determined that the properties of kaolins found in Afyon Alayurt are similar to those of kaolins obtained from Balıkesir Sındırgı region in terms of SiO_2 and Al_2O_3 contents, but the SO_3 content of kaolins in Afyon region is very low (Celik, 2010). Istanbul's Şile region has lower SiO_2 and higher Al_2O_3 contents than the kaolins from the Afyon region. SO_3 contents do not differ. It is stated that both kaolin samples are suitable for use in ceramic production (Celik, 2010).

When compared with kaolins used in the ceramic sector and in great demand in the sector, it is seen that the SiO_2/Al_2O_3 ratios of kaolins from Bulgaria, England (Bauer & Berger, 1998) and Ukraine (Eygi, 2009) are very close to the ideal ratio of 1.18, and they do not contain both coloring and polluting compounds such as Fe_2O_3 and SO_3. It becomes obvious that enrichment of the samples collected from the Balkesir Sındırgı region is required when compared with kaolins, which can be used in different areas according to their chemical contents and mineral compositions.

3. Literature review

The enrichment of alunitic kaolins can be grouped under four main headings, considering the literature.

Some researchers tried to separate alunite from kaolin using physical methods such as washing-dispersion, magnetic separation, and hydrocyclone enrichment, but they were not successful with these methods (Sayın, 1995; Yapa, 1993; Day, 1996; Day & Toroğlu, 1997; İpekoğlu & Kurşun, 1999; Erkan, 2002). On the other hand, coarse quartz and iron with magnetic properties can be removed by using these methods. İpekoğlu & Kurşun (1999) first mechanically dispersed Çanakkale Tepeköy Dumanlı kaolins and then tried to enrich them with hydrocyclones. In this way, the SiO_2 content was reduced from 60.72% to 47.6%.

In another method of beneficiation based on physico-chemical properties, flotation, flocculation, or both methods are used. Koca & Koca (2000) tried to remove alunite from kaolin ore by flotation using a carrier mineral (calcite). They obtained kaolin concentrate with 1.03% SO_3 content from kaolin ore with 8.03% SO_3 content and 57.95% kaolin yield. Ustuer & Gürgey (1975) tried to remove alunite from artificially formed alunite and kaolin minerals by selective flocculation. As a result, they obtained concentrates with 5.13% SO_3 content after 1st selective flocculation, 1.01% SO_3 content after 2nd selective flocculation, and 0.19% SO_3 content after 3rd selective flocculation from alunite clays with 21.68% SO_3 content. Yapa (1993) tried to recover Balıkesir-Bağkıran, Çanakkale-Sarıbeyli and Bursa-Mustafakemalpaşa alunitic kaolins by flotation method using sodium oleate and obtained concentrates with 0.22%, 0.36%, and 1.99% SO_3 content with kaolin yields of 73.7%, 66%, and 28.6%, respectively. Apart from these, some researchers have tried to remove alunite from kaolin by using flotation and selective flocculation together (Koca & Özdağ, 1994; Abdel-Khalek et al., 1996; Gebhardt, et al., 1998; Tatar, 2012).

Veglio et al. aimed to remove iron content from kaolin ores using sulfuric acid (H_2SO_4) and various organic acids (Veglio et al., 1993; Veglio et al., 1996; Veglio 1997; Veglio et al., 1998). They also examined the effect of experimental parameters and obtained iron removal efficiencies up to 98%. Many researchers have also investigated the effects of H_2SO_4 and organic acids on the removal of iron content from kaolin ore (Ambikadevi & Lalithambika, 2000; Saikia et al., 2003; Calderon et al., 2005; Lee et al., 2006). Arslan & Bayat (2009) used oxalic acid for the removal of iron from kaolin and also investigated the effect of solid-liquid ratio, temperature, and acid concentration parameters on iron solubility. As a result of the experiments, they determined that temperature and solid-liquid ratio were effective parameters. In the chemical dissolution experiments carried out under optimum conditions, they determined the Fe_2O_3 removal efficiency to be 94.89%. Çiftlik (2010) aimed to remove iron from kaolin by using one-stage oxalic acid and two-stage sulfuric acid + oxalic acid dissolution methods. As a result of the study, Fe_2O_3 removal was determined to be 35.51% as a result of one-stage dissolution, and Fe_2O_3 removal was determined to be 36.95% as a result of two-stage dissolution.

Although dissolution processes using acids are generally used to remove the iron content in kaolin ore, there are also studies using acids to obtain aluminum from alunite (Nazarov et al., 2001; Özdemir & Çetişli, 2005a). Özdemir & Çetişli (2005a) aimed to obtain Al from alunite ore by using acids such as H_2SO_4 at concentrations of 0.25-3M and hydrochloric acid (HCl) at concentrations of 0.5-0.6M in alunite ore calcined at different times and temperatures. Accordingly, the highest Al dissolution yields of 85% for H_2SO_4 and 83% for HCl were obtained at 95 °C dissolution temperature, 1.5M acid concentration for H_2SO_4 or 3M acid concentration for HCl, 76 µm average grain size, and 60 min at 650°C calcination temperature. Acids are also used to obtain aluminum from alunite as well as kaolin ore (Al-Zahrani & Abdul-Majid, 2009; Carroll & Starkey, 1971).

Ekmekçi et al. (2001) aimed to remove sulfate from the alunite kaolin structure by using sodium carbonate (Na_2CO_3). They were able to reduce the 1.53% SO_3 content to 0.75% in their dissolution studies at pH 12-13 at 60-65 °C temperatures. Luo et al. (2017a) aimed to dissolve alunite using potassium hydroxide (KOH) from flotation process waste containing kaolinite, alunite, dickite, and quartz. As a result of the study, all of the alunite in the flotation process wastes could be removed without damaging other minerals during dissolution at 90 °C for 30 minutes at a concentration of 13.5M KOH. In another study by Luo et al. (2017b), it was aimed to obtain potassium and aluminum from alunite wastes with an average grain size of 37.25 microns (µm) using KOH. As a result of their optimization studies, they reported that 99.5% of potassium, 84% of aluminum, and 5.6% of silicon could be dissolved at a solvent-solid ratio of 3.3% by mass, a temperature of 81.3 °C, 41.6 minutes, and a KOH concentration of 53.9% by weight, while other minerals, kaolinite and quartz, remained in the structure (Luo et al., 2017b).

Another method frequently used in the enrichment of alunitic kaolins is thermo-chemical. In these methods, alunitic kaolins are first heat treated, and then sulfate is removed by dissolution. Girgin et al. (1993) heat-treated alunitic kaolins with Na_2CO_3 and sodium chloride (NaCl) in order to reduce the SO_3 content of alunitic kaolins with high SO_3 content and then dissolved them with water. After roasting at 600 ºC, they obtained a concentrate with 0.48% SO_3 content from kaolin ore with 7.15% SO_3 content. As a result of a study conducted in our country on Balıkesir-Mustafa Kemal Paşa alunite kaolin with 12.73% SO_3 content, it was claimed that the calcined product with 2.14% SO_3 content obtained at 900 ºC could be used in the ceramic industry (Sümer, 1991). Ekmekçi et al. (2001) first enriched İvrindi alunite kaolin with 1.14% SO_3 content with a hydrocyclone to reduce the iron content and obtained a product with 1.53% SO_3 content, and then after flotation tests they obtained a product with 1.06% SO_3 content. They obtained concentrates with 1.04% SO_3 content after dissolution with sulfuric acid (H_2SO_4) at 60-65 ºC, 0.75% SO_3 content after dissolution with sodium carbonate (Na_2CO_3) at 60-65 ºC and 0.48% SO_3 content after roasting at 1000ºC. In a study by Genç (1994), the usability of kaolin with alunite as a raw material in the ceramic and refractory industries was investigated. For this purpose, he subjected alunite kaolin + salt mixtures to heat treatment at 500-900 ºC temperature ranges, dissolved the products degraded as a result of heat treatment in hot water, and tried to take all the sulfate in the structure into solution as potassium sulfate and sodium sulfate. Thus, they obtained a calcination product with 1-1.5% SO_3 content. Alpar et al. (1973) conducted ceramic test studies on the calcined product as a result of the calcination of clays containing alunite at 800 °C. H_2SO_4, potassium sulfate (K_2SO_4), and ammonium sulfate ($(NH_4)_2SO_4$) were chemically produced as a result of thermally treating alunite at 500–600 °C. Hoşgün et al. (1997) examined the dissolution kinetics of kaolin under acidic and alkaline conditions and found that 94% of Al_2O_3 was dissolved from kaolin treated with 10M HCl for 5 hours after calcining at 750 °C.

Alpar et al. (1973) used water dissolution, sodium silicate (Na_2SiO_3), sodium phosphate (Na_3PO_4), Na_2CO_3, and H_2SO_4 to remove sulfate from İvrindi kaolin within the scope of a research project, and as a result, they found that water could not be used for sulfate removal. They found that Na_2SiO_3 at 5% concentration provided 57.5% SO_3 removal at 80 °C, Na_3PO_4 at 5% concentration provided 56.9% SO_3 removal, and Na_2CO_3 at 5% concentration provided 63.2% SO_3 removal. The researchers also obtained 56.1% SO_3 removal efficiency in their experiments using H_2SO_4. They also carried out roasting experiments at 800 °C and found that the SO_3 content decreased to 0.26%, but the structure of kaolin deteriorated during this process.

Özdemir (1995), removed sulfate by 95% and reduced the sulfate content below 1% by dissolving the products obtained as a result of the thermal degradation of alunite kaolin ore at 700 ºC using KOH and potassium chloride (KCl) in water at 75 ºC. A similar study was conducted by Çetişli et al. (1993).

In his study, Yılmaz (2008) applied thermal treatments using NaCl and KCl salts at 600-1000 ºC using alunite kaolin with 9.45% SO_3 content. As a result, kaolin with 0.28% SO_3 content was obtained by thermal degradation at 1000 ºC. However, in all of the heat treatment methods, a meta-kaolinite phase was formed, which negatively affected the casting properties. Therefore, the use of these methods has negative consequences for the ceramic industry. Özdemir & Çetişli (2005b) aimed to remove sulfate from kaolin by mixing kaolin dry with KCl and KOH, then calcining and leaching in purified water. They obtained the best sulfate removal values with a removal efficiency of 97% after dry mixing 17.8% of kaolin ore with KCl and kaolin with alunite and calcining at 700 °C. They reduced the sulfate content of the alunitic kaolin ore from 12.97% to 1%.

Tatar (2012), in a study in which she tried to obtain products from kaolin with alunite using different beneficiation methods, was able to successfully remove the coloring oxides by mechanical dispersing-sieving and gradual grinding-sieving methods while reducing the SO_3 content from 4.05% to 3.44%. After this stage, she conducted flotation studies to produce a concentrate that she employed as a pre-enrichment stage. This concentrate had a recovery efficiency of 18.39%, a SO_3 concentration of 1.35%, and a mass ratio of 50.67%.

4. Conclusions

The basis of this study is to examine the sectoral utilization potentials of kaolin in the Balıkesir Sındırgı region, which contains a large amount of kaolin reserves in our country. In this direction, the usage areas of kaolin, and the standards determined according to the sectors were examined, and the importance of kaolin for the economy of our country was emphasized.

The suitability of four samples supplied from Balıkesir Sındırgı region with different chemical contents for industrial use was investigated by chemical and mineralogical analyzes, and the results were compared with the standards specified according to the sectors.

It has been determined that the kaolin samples supplied from the region are not suitable for use in the ceramic, paint, or paper industries in their raw form, and it has been concluded that the samples should undergo enrichment processes.

In particular, it was determined that the kaolins found in this region are also rich in alunite minerals, and the use of these kaolins in the industry will be a problem due to the sulfate content of the alunite minerals.

In addition, the enrichment methods of kaolins obtained from this and other regions were examined by reviewing the studies in the literature, and in light of this information, alternative enrichment methods that will shed light on future studies for the enrichment of kaolins in the Balıkesir Sındırgı region were put forward.

Acknowledgement

This research is a section of Dr. İlker Erkan's doctoral dissertation, "Extraction of Sulphate (SO_4^{-2}) from Balıkesir Sındırgı Alunitic Kaolins Using NaOH" which is supported by the Karadeniz Technical University's Scientific Research Projects unit through the 9022 coded "NaOH Liçi ile Kaolenden Sülfat Uzaklaştırılması" project.

Author contribution

Concept/Design, Data Collection, Processing, Literature Search, Drafting manuscript: IE;
Concept/Design, Critical revision of manuscript: IA

Declaration of ethical code

The authors declare that all of the rules stated to be followed within the scope of the "Higher Education Institutions Scientific Research and Publication Ethics Directive" were followed, and none of the actions specified under the title of "Actions Contrary to Scientific Research and Publication Ethics" have been carried out.

Conflicts of interest

The authors declare that they have no conflict of interest.

References

Abdel-Khalek, N.A., Omar, A.M.A., & Hassan Y. (1996). Froth flotation of ultrafine Egyptian kaolin ore. In M. Kemal, V. Arslan, A. Akar, & M. Canbazoglu (Eds), *Changing Scopes in Mineral Processing,* (pp. 395-400). AA Belkama, Rotterdam.

Akdeniz, N., & Konak, N. (1979). Rock units of the Menderes Massif around Simav and location of metabasic and metaultrabasic rocks. *TJK Bulletin*, *22*, 175-184. (in Turkish).

Alpar, S.R., Gürgey, İ., Rodopman, K., & Ustaer, C. (1973). *Treatment of sulfate and pyrite containing kaolin minerals*, TÜBİTAK, Engineering Research Group, MAG-246. (in Turkish).

Al-Zahrani, A.A., & Abdul-Majid, M.H. (2009). Extraction of alumina from local clays by hydrochloric acid process. *Journal of King Abdulaziz University: Engineering Science*, *20*(2), 29-41.

Ambikadevi, V.R., & Lalithambika, M. (2000). Effect of organic acids on ferric iron removal from iron-stained kaolinite. *Applied Clay Science, 16*, 133-145.

Arslan, V., & Bayat, O. (2009). Upgrading of kaolin ores by chemical leaching and bioleaching methods. *Kibited, 1*(3), 175-184. (in Turkish).

Bauer, A., & Berger, G. (1998). Kaolinite and smectite dissolution rate in high molar KOH solutions at 35° and 80°C. *Applied Geochemistry, 13*(7), 905-916.

Bayraktar, İ., Ersayın, S., Gülsoy, Ö. Y., Ekmekçi, Z., & Can, N. M. (1999). Temel seramik ve cam hammaddelerimizdeki feldispat kuvars ve kaolin kalite sorunları ve çözüm önerileri. *3rd Industrial Raw Materials Symposium* (pp.22-33), Ankara. (in Turkish).

Calderon, G.D.T., Rodriguez, J.I., Ortiz-Mendez, U., & Torres-Martinez, L.M. (2005). Iron leaching of a Mexican clay of industrial interest by oxalic acid, *Journal of Materials Online, 1*, 1-8.

Carroll, D., & Starkey, H.C. (1971). Reactivity of clay minerals with acids and alkalies. *Clays and Clay Minerals, 19*, 321-333.

Celik, H. (2010). Technological characterization and industrial application of two Turkish clays for the ceramic industry. *Applied Clay Science, 50*, 245-254.

Çiftlik, S. (2010). *Removal of metals from kaolin ores by using leaching method*, [MSc Thesis, Süleyman Demirel University, Science and Technology Institute]. (in Turkish).

D.P.T. (1995). *Yedinci Beş Yıllık Kalkınma Planı (1995-1999). Madencilik Özel İhtisas Komisyonu Endüstriyel Hammaddeler Alt Komisyonu Raporu*, Devlet Planlama Teşkilatı. Yayın No, 2418/477, Başbakanlık Basımevi, Ankara.

D.P.T. (2001). *Sekizinci Beş Yıllık Kalkınma Planı (2001-2005). Madencilik Özel İhtisas Komisyonu Raporu*, Devlet Planlama Teşkilatı. Yayın No: 2611/622, Başbakanlık Basımevi, Ankara.

Day, N., & Toroğlu, I. (1997). Bilecik (Sögüt) yöresi killerinin AKW hidrosiklonu ile zenginleştirilmesi. *2nd Industrial Raw Materials Symposium* (pp. 187-192), Izmir. (in Turkish).

Day, N. (1996). *Kaolinite beneficiation with hydrocyclone* [MSc Thesis, Zonguldak Karaelmas University, Science and Technology Institute]. (in Turkish).

Demirbilek, F. (2007). The change in the physical characteristics, mineralogic structure and plasticity of kaolin and illite ceramic clays [MSc Thesis, Dumlupınar University, Science and Technology Institute] (in Turkish)

Demirtaş, G. (2011). Analaysing the being fried properties of Balıkesir-Sındırgı-Düvertepe alunitic kaolin with different contents of alunite [MSc Thesis, Dumlupınar University, Science and Technology Institute] (in Turkish)

Ece, I., & Yüce, A.E. (1999). *Kaolin.* Istanbul Mineral Exporters Association. (in Turkish).

Ece, Ö.I., & Ekinci, B. (2009). *Tektonik Olarak Aktif Simav Grabeni Boyunca Oluşan Düvertepe Kaolin-Alunit Yataklarının Mineralojik-Jeokimyasal Değişimi ve Orijini*, TUBİTAK ÇAYDAĞ-106Y070, İstanbul. (in Turkish).

Ekinci, B. (2009). *Geological, mineralogical and geochemical investigation of kaolin (+/- alunite) occurrences in Düvertepe-Şapçi regions (Sındırgı, Balıkesir)* [MSc Thesis, Istanbul Technical University, Science and Technology Institute]. (in Turkish).

Ekmekçi, Z., Gülsoy, Ö., Ersayın, S., & Bayraktar, İ. (2001). Desulphurisation of İvrindi alunitic kaolin, *Yerbilimleri, 23*, 53-60.

Elmacı, M. (1989). *Balıkesir İli-Sındırgı İlçesi-Düvertepe Nahiyesi Güneyi ve Çıkrıkçı Kuzeyi ÖİR 1930 No'lu M.T.A. Alüminyum (Kaolen) Ruhsatlı Sahasına Ait Maden Jeolojisi Raporu*. M.T.A. Report No: 2889. (in Turkish).

Erkan, Z.E. (2002). *Balıkesir – Sındırgı Düvertepe bölgesi Döküştepe mevkii kaolin cevherinin zenginleştirilmesi* [MSc Thesis, Dokuz Eylül University, Science and Technology Institute]. (in Turkish).

Eygi, M.S. (2009). *Improving the usage of kaolin in ceramic with the aid of polyelectrolyte* [PhD Thesis, Istanbul Technical University, Science and Technology Institute]. (in Turkish).

Gebhardt, J.E., Piga, L., & Schena, G. (1998). Flocculation and flotation behavior of a low-grade alunite ore, *Minerals and Metallurgical Processing, 15*(4), 48-52.

Genç, S. (1994). *Sulphate removal from alunite kaolins and production of ceramic raw material* [PhD Thesis, Osmangazi University, Science and Technology Institute]. (in Turkish).

Girgin, Ü., Ekmekçi, Z., & Erkal, F. (1993). Sındırgı alunitli kaolini zenginleştirme çalışmaları. *13th Mining Congress of Turkiye* (pp. 549-560), İstanbul. (in Turkish).

Güneş, A.N., Akçil, A.U., Çiftlik, S., & Handırı, İ. (2009). *Kaolinlerin organik asitler kullanılarak liç yöntemiyle saflaştırılması*. TUBİTAK, Project No: 108M180. (in Turkish).

Hoşgün, H.L., Altıokka, M.R., & Çıtak, A. (1997). Kaolinin HCl ve NaOH çözeltilerinde çözünme kinetiğinin incelenmesi, *8th National Clay Sympossium* (pp. 195-204), Kütahya. (in Turkish).

İpekoğlu, B., & Kurşun, I. (1999). Dumanlı kaolinlerin zenginleştirilmesi, *3rd Industrial Raw Materials Symposium* (pp. 16-21), İzmir. (in Turkish).

Koca, S., & Koca, H. (2000). Carrier flotation of alunite from kaolin clay. *XXI. International Mineral Processing Congress* (pp. 1-8), Italy

Koca, S., & Özdağ, H. (1994). Flotation of alunite from kaolin, progress in mineral processing technology, A.A. Balkema, Rotterdam.

Lee, S.O., Tran, T., Park, Y.Y., Kim, S.J., & Kim, M.J. (2006). Study on the kinetics of iron oxide leaching by oxalic acid. *International Journal of Mineral Processing, 80*, 144-152.

Luo, M-J., Liu, C-L., Jiang, Y., Xue, J., Li, P., & Yu, J-G. (2017b). Green recovery of potassium and aluminium elements from alunite tailings using gradient leaching process. *Journal of Cleaner Production, 168*, 1080-1090.

Luo, M-J., Liu, C-L., Xue, J., Li, P., & Yu, J-G. (2017a). Leaching kinetics and mechanism of alunite from alunite tailings in highly concentrated KOH solution. *Hydrometallurgy, 174*, 10-20.

Nazarov, Sh. B., Gulakhmadov, Kh. Sh., Khakdodov, M.M., & Aminov, Sh. G. (2001). Processing of aluminum sulfates into alumina. *Russian Journal of Applied Chemistry, 74*(8), 1392-1394.

Oygür, V. (1997). Anatomy of an epithermal mineralization: Mumcu (Balıkesir-Sındırgı), inner-western Anatolia, Turkey. *Bulletin of The Mineral Research and Exploration, 119*, 29-39.

Özdemir, M., & Çetişli, H. (2005a). Extraction kinetics of alunite in sulfuric acid and hydrochloric acid. *Hydrometallurgy, 76*, 217-224.

Özdemir, M., & Çetişli, H. (2005b). Sulphate removal from alunitic kaolin by chemical method. *Industrial & Engineering Chemistry Research, 44*, 3213-3219.

Özdemir, M. (1995). *The removal of sulphate from alunitic kaolins by chemical method the utilization in potassium sulphate and aluminum sulphate production* [PhD Thesis, Osmangazi University, Science and Technology Institute]. (in Turkish).

Saikia, N.J., Bharali, D.J., Segupta, P., Bordoloi, D., Goswamee, R.L., Saikia, P.C., & Borthakur, P.C. (2003). Characterization, beneficiation and utilization of a kaolinite clay from Assam, India. *Applied Clay Science, 2*, 93-103

Sayın, S.A. (1995). Kaolinit içeren kil yataklarının hidrosiklon ile zenginleştirilmesi. *7th National Clay Symposium*, Ankara. (in Turkish).

Sümer, G. (1991). *Alunitli Kaolinlerin Zenginleştirilmesi* [MSc Thesis, Anadolu University, Science and Technology Institute]. (in Turkish).

Tatar, İ. (2012). *Determination of usage areas of the products obtained from alunitic kaolins by means of different enrichment approaches* [PhD Thesis, Dumlupınar University, Science and Technology Institute]. (in Turkish).

TUİK. (2020). *Import-Export Data of Kaolin*, Turkish Statistical Institute. (in Turkish).

Tunçay, N.Ö. (2006). *A linear programming model implementation for mine mixture and transportation costs minimization with acase study* [MSc Thesis, Balıkesir University, Science and Technology Institute]. (in Turkish).

Ustuer, C., & Gürgey, I. (1975). The separation of alunite in alunitic kaolin by selective flocculation. *Clays and Clay Minerals, 23*, 468 472.

Veglio, F. (1997). Factorial experiments in the development of a kaolin bleaching process using thiourea in sulphuric acid solutions. *Hydrometallurgy, 45*, 181-197.

Veglio, F., Pagliarini, A., & Toro, L. (1993). Factorial experiments for the development of a kaolin bleaching process. *International Journal of Mineral Processing, 39*, 87-99.

Veglio, F., Passariello, B., Barbaro, M., Plescia, P., & Marabini, A.M. (1998). Drum leaching tests in iron removal from quartz using oxalic and sulphuric acids. *International Journal of Mineral Processing, 54*, 183-200.

Veglio, F., Passariello, B., Toro, L., & Marabini, A.M. (1996). Development of a bleaching process for a kaolin of industrial interest by oxalic, ascorbic, and sulphuric acids: preliminary study using statistical methods of experimental design. *Industrial & Engineering Chemistry Research, 35*, 1680-1687.

Yapa, N. (1993). *Alunitli Kaolinlerin Değerlendirilmesi* [PhD Thesis, Istanbul Technical University, Science and Technology Instituite]. (in Turkish).

Yılmaz, B. (2008). *Sulphate removal from alunite kaolines and production of ceramic raw material* [MSc Thesis, Osmangazi University, Science and Technology Institute]. (in Turkish).

Yılmaz, H. Ö., & Günen, M. A. (2023). Is environment destiny? Spatial analysis of the relationship between geographic factors and obesity in Türkiye. *International Journal of Environmental Health Research*, 1-13.